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TRW Defense and Space Systems Group, Redondo Beach, Calif

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TECHNICAL MANUAL FOR MONITORING SAMPLING AND ANALYSIS



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FOR INORGANIC SAMPLING
AND ANALYSIS**

by

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INTRODUCTION

This technical manual has been prepared for the Industrial and Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina, in partial fulfillment of Task 16 of Contract #58-02-1412. The manual is written for personnel who are experienced in collecting and analyzing samples from industrial and energy producing processes. This manual includes general introductions to a variety of sampling and analysis procedure categories as well as abstracts on each specific method.

A. DESIGN OF MANUAL

This technical manual presents the state of the art of Inorganic Sampling and Analysis (ISA) procedures in a standardized format that makes methodology readily available to the professionals in the field. Because of the breadth of ISA, a system was developed to avoid burying specific methods in an avalanche of narrative. This design concept makes the techniques of sampling and analysis easily accessible, while providing a comprehensive, cross-referenced index of process stream and chemical test situations, and procedures.

The sampling and analysis procedures in this manual are compatible with either environmental assessment or process measurement activities. The intent of this manual is to provide a compilation of methods applicable to these activities. The methods included in this manual generally are proven procedures from standard sources. In many cases, where gaps in sampling or analysis procedures existed, the open literature and government reports were combed for appropriate methods.

B. ORGANIZATIONAL OUTLINE

An eight-digit identification number is assigned to each sampling and analysis method. The eight-digit identification (ID) number is designed to cross-reference particular methods with the procedures associated with the sampling phase and the analysis phase. The identification number functions as follows. The first pair of digits of the ID number represents either the sampling phase (designated 01) or the analysis phase (designated 02). The phases are subdivided into process stream and chemical test categories

(represented by the second pair of digits in the ID number) which have procedures associated with them (represented by the third pair of digits of the ID numbers). For each type of procedure there are specific examples of implemented methods (designated by the fourth pair of digits in the ID number), presented as abstracts. The abstract will provide enough information to allow the measurement professional to decide whether or not the method meets his needs. The abstract sheets contain a primary reference that provides the reader with all the information required to implement the procedure.

Each abstract contains the following information:

- 1) TITLE. The title is either a description of the technique, or the specific name of the technique if it is from a standard source.
- 2) IDENTIFICATION CODE. This can be up to an eight-digit number which signifies the procedural category grouping of the specific technique.
- 3) ABSTRACT OF METHODOLOGY. This section describes the key steps of the laboratory preparation or procedure involved in a particular sampling analysis. References to other pertinent abstracts are included.
- 4) APPLICATION (HEADING). These headings are the possible use categories and will be arranged in descending order of applicability. The categories are: Compliance, Engineering Evaluation R&D and Environmental Assessment.
The compliance category contains most of the EPA approved methods for water [Federal Register, 41 (232), 52780 (1976)] and air [Federal Register, 41 (111), 23061 (1976)]. The environmental assessment methods are those approved methods found in J.W. Hamersma, S. L. Reynolds and R. F. Maddalone "IERL-RTP Procedures Manual: Level 1 Environmental Assessment", TRW Systems Group, EPA 600/2-76-160a, June 1976. The Engineering Evaluation R&D methods are taken from a variety of sources and provide sampling and analysis alternatives to meet specific measurement problems. These categories are not meant to restrict the use of the methods to the specific applications, but are meant to be a guide to their source and primary use.
 - a) Operational Scope: Describes the possible process streams to which these specific techniques or methods can be applied.

- b) Interferences/Limitations: Describes the chemical or physical interferences or limitations of the abstracted procedure.
- c) Recommended Use Area: Specifies the intended use of the method.
- 5) OPERATIONAL PARAMETERS.
 - a) Range: Lists the working range and sensitivity (2σ) of the method.
 - b) Accuracy: Gives the actual stated accuracy, or an estimated value if no value is stated (N/Q).
 - c) Precision: Gives either quoted or estimated precision values.
- 6) REAGENTS REQUIRED. Under this heading specific reagents required for the analysis or sampling method are listed.
- 7) EQUIPMENT REQUIRED. The specific equipment needs (as well as sources in many cases) are listed.
- 8) KEYWORD INDEX. Normally a set of three keywords is listed. The first describes the general use area, the second the major category area, and the third the specific technique.
- 9) CROSS-REFERENCE ID NUMBERS. This section lists the identification numbers and auxiliary techniques that either complement or complete the abstracted procedure. For example, "Sampling flue gas for trace inorganic materials" (01-04-01-01) will cross-reference specific handling procedures for removal of particulates on filters (02-01-03-04), removal of particulates from cyclones (02-01-03-05) and removal of particulates from probe liners (02-01-03-06).
- 10) REFERENCES:
 - a) Primary Source: Specifies the reference that was used to provide the information for the format page. For example, if an ASTM method was summarized, the specific ASTM reference would be given.
 - b) Background Information: Presents any references that would be useful for the analyst in the operation of the instrument or the completion of chemical analysis.
 - c) Field Applications: Provides field applications references to give the current use or uses of the particular technique described.

C. BENEFITS OF THIS APPROACH

This system fulfills the need for general concepts while allowing:

- Easy review and update--Rather than rewriting extensive narrative, each abstract is readily corrected or updated separately.
- Multidimensional expansion--Because the format is designed as a four-level branching network, major categories and specific examples can be added as appropriate. Furthermore, the exact instructions can be printed on a continuation sheet and inserted behind the abstract sheet.
- Cross-reference access to procedures--Since each abstract is keyworded, a thesaurus of keyword ID numbers can be developed.
- Recommended methods can be clearly identified--Since each procedure is in abstract form, either a list of ID numbers or color-coded pages can be used to specify recommended procedures.
- Readily used as source for procedure manuals--Individual abstracts for specific process sampling and analysis needs can be rapidly assembled as a "rough draft" to form a procedures manual. From this assemblage of abstracts, a smooth narrative can be written using the information and figures provided in the abstracts. The abstracts are then kept in an appendix as a source of reference.

Thus, this technical manual is designed to be a living document, one that can be continually updated, revised and expanded simply by changing or adding abstract sheets.

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01-01-02-01 Sampling Flue Gases Using Direct Reading Gas
Detection Tubes

01-01-02-02 SO₂ Adsorption on Solids (Silica Gel)

01-01-03 Condensation Techniques

01-01-03-01 Sulfur Oxides in Flue Gas by Controlled
Condensation (Goksoyr-Ross Method)

01-01-04 Gas Grab Sampling

01-01-04-01 General Gas Grab Sampling Techniques

01-01-04-02 Flue Gas Grab Sampling Using Plastic Bags

01-01-04-03 High Pressure Gas Grab Sampling (Natural Gas
Containing Hydrocarbons and Nitrogen, Sulfur)

APPLICATION MATRIX FOR 01-01 SAMPLING GAS/VAPOR IN FLUE GAS

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
01-01-01-01		●	●
01-01-01-02		●	●
01-01-01-03			●
01-01-01-04		●	●
01-01-01-05			●
01-01-01-06		●	
01-01-01-07		●	
01-01-01-08		●	
01-01-01-09		●	
01-01-02-01	●		
01-01-02-02	●		●
01-01-03-01	●		●
01-01-04-01	●		●
01-01-04-02	●		●
01-01-04-03	●		●

SAMPLING GASES OR VAPORS IN FLUE GAS - ID No. 01-01

This section will discuss the sampling of gases or vapors in flue gas streams. The techniques employed are absorption in liquids, adsorption on solids, condensation and grab sampling. No one specific technique is best for all situations, but on the basis of use, absorption in liquids is the most popular, followed by grab sampling.

Recent studies (reference 001) have shown that a high degree (10-20%) of stratification of gases occurs in flue gas ducts. Consequently, gas sampling requires techniques similar to particulate sampling. The exception to this comparison is that gas sampling does not require isokinetic flow rates to obtain a representative sample, but standard procedures (reference 002) should be used to choose a representative sampling point.

The point of this discussion is that each method has its limitations. No one method will fulfill all sampling needs. The analyst, by understanding the benefits and drawbacks of each procedure, will make the right choice for a given sampling task.

01-01-01 Absorption in Liquids (Abstracts 01-01-01-01 Through 01-01-01-05)

Absorption of gases in a liquid bath retains and concentrates the contaminant for subsequent analysis. The flow rate will depend on the equipment used. Typical flow rate values for various liquid absorbing systems are: 2 lpm for fritted bubblers, 2.8 lpm for midjet impingers, 28 lpm for Greenburg-Smith impingers, and 140 lpm for impingers found in high volume stack samplers (see 01-04-01-02).

The efficiencies of these collection devices typically run between 95 to 99% for reactive collection media (for example 3% H_2O_2 for SO_2 , see 01-01-01-01). These efficiencies are influenced by several factors:

- 1) Solubility of contaminant in collection medium - Normally, reactive media are chosen to prevent escape of absorbed gases.
- 2) Rate of diffusion into the medium - This is partially influenced by temperature and bubble size which depends on flow rate and choice of impinger.

- 3) Vapor pressure of contaminant at sampling temperature - Normally ice baths are used to cool gases and reduce volatility.
- 4) Chemical reactivity of contaminant with sampling medium - Reaction rate is the most important variable. The contaminant must react faster than it can be revolatilized (01-01-01-02).
- 5) Flow rate - The flow rate will affect contact time in the bubbler and because of the above considerations will directly affect efficiency.

Finally, the prime consideration when using liquid absorbers is to select a medium which does not interfere with any subsequent analysis. In all cases, the analyst must be aware of the ultimate goal of the sampling task so that the choice of sampling system does not complicate or invalidate the final analysis of the collected sample. For example, if compound identification is the ultimate goal of the sampling task, collection of Hg and $(CH_3)_2 Hg$ in an oxidative scrubber (01-01-01-02, 01-01-01-05) will destroy the compounds and yield the total Hg content of the stream. Either grab sampling or selective adsorption would be a better choice.

01-01-02 Adsorption on Solids (Abstracts 01-01-02-01 Through 01-01-02-03)

Adsorption on solid media and in particular silica gel for inorganic compounds provides a viable alternative to liquid absorption. Silica gel or molecular sieve packing materials adsorb inorganic gases readily while allowing quantitative removal back in the laboratory. Silica gel has found extensive use (see 01-01-02-01) as a support medium for direct reading colorimetric sampling tubes (reference 003). As with liquid absorption, several factors (reference 004) can affect the efficiency of solid adsorbents:

- 1) Previous history of the gel - The silica gel is usually cleaned by heating in a nitrogen atmosphere at 350 to 400°C.
- 2) Size of gel particles - The smaller the particle size, the greater the surface area for adsorption, but the higher the pressure drop. Normally, a gel size range of 6 to 28 mesh is satisfactory, provided a narrow (6-16 or 14-28) range of particles is actually used.

- 3) Amount of gel particles - The bed depth and mass of silica gel used ultimately affects the capacity and efficiency of the adsorbing system. The minimum diameter of the adsorbing column should be several times larger than the diameter of the gel to prevent channeling.
- 4) Flow rate - This is a difficult variable to assess and probably will depend on the species being adsorbed as well as the chemical reaction (if impregnated silica gel is used). Nominal linear flow rates are from 50 to 1000 cm/min.
- 5) Temperature - In most cases, this variable should be kept as low as possible. Normally, room temperature is sufficient. Direct reading colorimetric tubes are useful up to 50°C.
- 6) Chemical reactions - One must always guard against unwarranted side reactions once the gas is adsorbed. In particular, oxidation of adsorbed SO₂ must be prevented by rapid analysis or storage under nitrogen.

Desorption of gases (SO₂, NH₃) adsorbed on silica gel (01-01-02-02, 01-01-02-03) is normally done by heating the adsorption tube in the presence of an inert gas flow. The gas can then be analyzed by liquid absorption or by instrumental techniques. Solid adsorption effectively concentrates the gas sample so the analyst has a much easier analysis task.

01-01-03 Gas Condensation Techniques (Abstract 01-01-03-01)

Condensation or freeze-out techniques are more useful for organic vapor sampling. Inorganic gases normally require too low of a temperature to make freeze-out techniques practical. Controlled condensation of a gas like SO₃ can be accomplished because of its affinity for water. This procedure is described in 01-01-03-01 and is recommended over Method 8 as the method of choice for SO₃ measurements. Recent studies (reference 005) have shown that 80% isopropanol picks up significant quantities of SO₂ which oxidizes in solution causing a positive error.

01-01-04 Flue Gas Grab Sampling (Abstracts 01-01-04-01 Through 01-01-04-03)

Grab sampling is the use of rigid or nonrigid containers for collecting a single point/single sample or multipoint/composite sample of gas

for subsequent laboratory analysis. For flue gas sampling plastic bags are not recommended, though they can be used under a narrow set of temperature and gas component conditions (see 01-01-04-02). For the most part, flue gas grab sampling will be accomplished using rigid containers made of glass or stainless steel (01-01-04-01, 01-01-04-03).

The key problem with grab sampling is the possibility of chemical changes occurring in or catalyzed by the sample container. Gas phase reactions do not stop once the gases are removed from the gas stream. In fact, removal from the gas stream probably will initiate reactions. For example, once the gas container is filled, the temperature will fall causing any excess moisture to condense. The condensation process can change the gas phase concentration of SO_2 , CO_2 or H_2S . If glass containers are used, photochemical reactions must be guarded against by keeping the container in a dark place prior to analysis.

The biggest problem with grab samples is the adsorption of gases onto the walls of the container. To a certain extent, the containers can be warmed prior to analysis or flushed with inert gas to remove any adsorbed gases. The preferred approach to this problem is to analyze the gas in the container as soon as possible after sampling.

Since the rigid containers will be reused, caution must be exercised to remove any last traces of the previous sample. Since the last gas sampled could conceivably activate the container walls to subsequent chemical reactions by the next gas sample, each container should be passivated by the appropriate technique prior to reuse (see 02-01-01-07).

REFERENCES

- 001 Brooks, E.F., C.A. Flegal, L.N. Harnett, M.A. Kolpin, D.L. Luciani and R.L. Williams, "Continuous Measurement of Gas Composition from Stationary Sources," EPA-600/2-75-012, TRW Systems, Redondo Beach, CA., July 1975.
- 002 Federal Register, "Method 1 - Sample and Velocity Traverses for Stationary Source," 36(247), 24882 (December 23, 1971).
- 003 Lechnity, K., "Detector Tube Handbook," 2nd ed., Dragerwerk-A-G-Lubeck, October 1973 (obtained from National Mine Service Co., Pittsburgh, PA.).
- 004 Ind. Hyg. Assoc., "AIHA Analytical Guides," 1965, p. 8-16.
- 005 Grant, A., D.L. Luciani and R.F. Maddalone, "Final Report for Process Measurements Development: Particulate Sulfate Emissions," TRW Systems, Redondo Beach, CA., EPA Contract No. 68-02-14-12, March 1975.

1. TITLE DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES		2. IDENTIFICATION CODE 01-01-01-01
3. ABSTRACT OF METHODOLOGY A gas sample is removed from the gas stream and the acid mist, including sulfur trioxide, is separated from the sulfur dioxide using a midget bubbler filled with 80 percent isopropyl alcohol. The resultant gas stream is passed through two midget impingers containing a 3 percent solution of H_2O_2 to remove the sulfur dioxide. The peroxide solution is titrated with barium perchlorate using thorin as the indicator (see 02-03-02-05).		
4. APPLICATION: Compliance, engineering evaluation R&D.		
A) OPERATIONAL SCOPE This procedure is designed to sample SO_2 from flue gas streams to determine compliance with New Source Performance Standards of the EPA.		
B) INTERFERENCES/LIMITATIONS Varying amounts of SO_2 can be collected in the isopropyl alcohol trap and cause negative results. The 80 percent IPA impinger should be purged with nitrogen into the 5 percent H_2O_2 impingers to remove any SO_2 absorbed in the IPA.		
C) RECOMMENDED USE AREA Compliance testing of stationary sources.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/Q (10 ppm lower limit estimated).		
B) ACCURACY $\pm 5\%$		
C) PRECISION $\pm 3\%$ or better.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Water (D.I.), isopropanol (80%), hydrogen peroxide (3%), thorin, barium perchlorate, sulfuric acid.		Glass probe, midget bubbler, glass wool, midget impinger, drying tube, needle valve, vacuum pump, rate meter, dry gas meter, laboratory glassware.
8. KEYWORD INDEX: Flue gas sampling, SO_2 sampling, compliance, sampling.		
9. CROSS REFERENCE ID NUMBERS 02-03-02-05,-06; 02-01-01, 03.		
10. REFERENCES		
A) PRIMARY SOURCE 006 Federal Register, "Determination of Sulfur Dioxide Emissions from Stationary Sources," 36(247), 24890 (1971).		
B) BACKGROUND INFORMATION 007 U.S. DEW, PHS, Div. of Air Pollution, "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes," PHS Publication No. 999-AP-13, Cincinnati, Ohio (1965). 008 Patton, W.F., and J.A. Brink, Jr., "New Equipment and Techniques for Sampling Chemical Process Gases," J.A.P.C.A., 13, 162 (1963).		
C) FIELD APPLICATIONS 009 Corbett, P.F., "The Determination of SO_2 and SO_3 in Flue Gases," J. Inst. Fuel, 24, 237 (1961). 010 Matty, R.E., and E.K. Diehl, "Measuring Flue Gas SO_2 and SO_3 ," Power, 101, 94 (1957). 011 Driscoll, J., J. Becker, R. Hebert, K. Horbal, and M. Young, "Validation of Improved Chemical Methods for Sulfur Oxides Measurements from Stationary Sources," Walden Res. Corp., Cambridge, Mass., PB215-887, November 1972. 012 Driscoll, J., and A.W. Berger, "Improved Chemical Methods for Sample and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels," Walden Res. Corp., Cambridge, Mass., PB209-267, June 1971.		

1. TITLE OXIDES OF NITROGEN IN GASEOUS COMBUSTION PRODUCTS BY THE PHENOL DISULFONIC ACID PROCEDURE		2. IDENTIFICATION CODE 01-01-01-02
3. ABSTRACT OF METHODOLOGY The gas sample is admitted into an evacuated flask containing an oxidizing absorbent consisting of hydrogen peroxide in dilute sulfuric acid. The oxides of nitrogen are converted to nitric acid by the solution. The NO_x as nitrate ion is reacted with phenol disulfonic acid to produce a yellow compound which is measured colorimetrically at 400 nm (see 02-03-02-20).		
4. APPLICATION: Compliance, engineering evaluation R&D.		
A) OPERATIONAL SCOPE This method can be used to measure the total oxides of nitrogen (N ₂ O excepted) in gaseous effluents from combustion and other nitrogen oxidation processes.		
B) INTERFERENCES/LIMITATIONS Inorganic nitrates, nitrites or organic nitrogen compounds that are easily oxidized to nitrates interfere with the method and give erroneous high results. Under conditions of high sulfur dioxide concentrations, care must be taken to ensure that there is enough hydrogen peroxide solution to absorb both the SO ₂ and the oxides of nitrogen. NOTE: ASTM admits that the role of some of the constituents of combustion effluents as possible interferences has not been thoroughly investigated as of 1974.		
C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE This method is applicable to a concentration range of oxides of nitrogen as nitrogen dioxide from 5 to several thousand parts per million.		
B) ACCURACY N/Q		
C) PRECISION ±1% for synthetic samples.		
6. REAGENTS REQUIRED Hydrogen peroxide, sulfuric acid, ammonium hydroxide, phenol disulfonic acid, potassium nitrate, sodium hydroxide.		7. EQUIPMENT REQUIRED Calibrated sampling flask, spectrophotometer, laboratory glassware, mercury manometer, pump (vacuum), water bath.
8. KEYWORD INDEX: Sampling, gas sampling, NO _x analysis.		
9. CROSS REFERENCE ID NUMBERS 02-03-02-20; 01-01-04.		
10. REFERENCES		
A) PRIMARY SOURCE 590 U. S. Environmental Protection Agency, FED. Reg., 41 (111), 23045 (1976).		
B) BACKGROUND INFORMATION 013 ASTM Standards, Part 26, "Standard Method of Tests for Oxides of Nitrogen in Gaseous Combustion Products (Phenol Disulfonic Acid Procedure)," 1974, p. 323.		
C) FIELD APPLICATIONS		

2. IDENTIFICATION CODE

1. TITLE HIGH PRESSURE GAS SAMPLING TRAIN (GASIFIER OUTPUT SAMPLING)

01-01-01-03

3. ABSTRACT OF METHODOLOGY

The sampling train (Figure 01-01-01-03A) consists of a modified ASTM liquid sampling probe, an impinger for condensing product water and oils in an ice bath under pressure, followed by pressure reduction and a second impinger series. The second set of impingers is designed for oxidative scrubbing of the sample to remove acid gases (Impinger No. 1, 3 M H_2O_2), trace metals absorption (Impinger No. 1, as above, and Impingers No. 2 and 3, consisting of 3 M hydrogen peroxide, 0.2 M $(NH_4)_2 S_2O_8$ and 0.02 M silver nitrate), and drying of the sampled gases (Impinger No. 4, containing Drierite). Gas sampling ports are included to obtain gaseous samples for analysis before and after trace metals scrubbing. Table 01-01-01-03A lists analyses which can be performed on collected samples.

4. APPLICATION: Engineering evaluation R&D.

A) OPERATIONAL SCOPE

The sampling train is applicable to gasifier output sampling involving temperatures up to and greater than 500°C, pressures up to and greater than 300 psig for acid gases, mists, and trace metals.

B) INTERFERENCES/LIMITATIONS

The test should be conducted under isokinetic conditions as far as possible, although this parameter is difficult to determine.

C) RECOMMENDED USE AREA

This is the recommended engineering evaluation R&D method for high pressure gas sampling.

5. OPERATIONAL PARAMETERS

- A) RANGE Method requires a sampling rate of 2 to 10 m^3 of gas over a 1- to 4-hour period, in order to detect 60 $\mu g/m^3$ of a given volatile trace element in the gas stream.
- B) ACCURACY 10-20% relative error.
- C) PRECISION $\pm 10\%$ or better.

6. REAGENTS REQUIRED

Impinger reagents (3 M hydrogen peroxide, 0.2 M hydrogen peroxide, 0.2 M nitric acid, 0.02 M silver nitrate, Drierite drying agent), ice.

7. EQUIPMENT REQUIRED

ASTM sampling probe, all metal condenser module fabricated from low carbon steel, standard impinger module; pressure gauges; sampling vessels; dry test meter; 20-40 meter exhaust hose.

8. KEYWORD INDEX: Gas sampling, impingers, ASTM liquid probe.

9. CROSS REFERENCE ID NUMBERS 02-02; 02-03; 02-04.

10. REFERENCES

A) PRIMARY SOURCE

- 014 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," TRW Systems Group, EPA Contract No. 68-02-1412, March 1975, p. 7-4.

B) BACKGROUND INFORMATION

- 015 ASTM Committee D-2 and F-7, "Petroleum Products-LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," 1971 Annual Book of ASTM Standards, Part 18, D270-65, "Sampling Petroleum and Petroleum Products," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 47-71.
- 016 Personal Communication, S. Gasior, U.S. Bureau of Mines to J.W. Hamersma, TRW Systems Group, February 24, 1975.
- 017 Personal Communication, D. Olsen, IGT-Hygas to J.W. Hamersma, TRW Systems Group, February 24, 1975.

C) FIELD APPLICATIONS

- 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Technical Manual for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975.

TITLE HIGH PRESSURE GAS SAMPLING TRAIN (GASIFIER OUTPUT SAMPLING) (CONTINUED)

ID NO. 01-01-01-03

Table 01-01-03-03A. Analysis of Gasifier Output (Reference 014).

Sample	Class	Analysis or Components	Principal Position in Sampling Train
Gases	Inorganic gases	H ₂ , CO, CO ₂ , O ₂ , N ₂	First Impinger Series; Gas Sampling Vessels
	Sulfur-containing gases	H ₂ S, SO ₂ , COS, CS ₂ , mercaptans, thiophenes	First Impinger Series; Gas Sampling Vessels
	Organic compounds	CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈ through higher boiling homologues.	First Impinger Series; Gas Sampling Vessels
Organic Liquids	Class analysis	A. Low boiling paraffins, aromatics, phenols, basic nitrogen compounds, and organosulfur compounds.	First Impinger Series
		B. High boiling paraffins, and organic material including PAH, neutral and basic nitrogen compounds, oxygen, and sulfur compounds.	First Impinger Series
	Trace elements	Ba, Be, Ca, Cd, Cr, Cu, F ⁻ , Hg, Mn, Ni, Pb, Sb, Se, Sr, Zn	Second Impinger Series
Water	Trace elements	Ba, Be, Ca, Cd, Cr, Cu, F ⁻ , Hg, Mn, Ni, Pb, Sb, Se, Sr, Zn.	Second Impinger Series
	Anions	CN ⁻ , Cl ⁻ , F ⁻ , S, NO ₃ ⁻ , SO ₄ ⁻	Second Impinger Series
	Ammonia	NH ₃	First Impinger Series; Gas Sampling Vessels

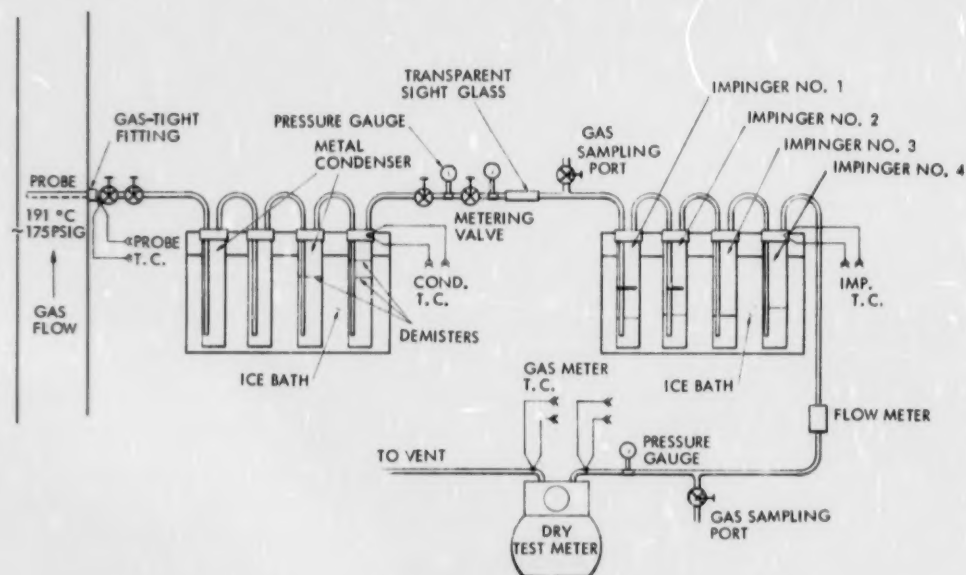


Figure 01-01-01-03A. Suggested Gasifier Sampling Train (Reference 014).

1. TITLE COLLECTION OF MERCURY IN GASEOUS EMISSIONS FROM STATIONARY SOURCES	2. IDENTIFICATION CODE 01-01-01-04
3. ABSTRACT OF METHODOLOGY Gaseous samples from a stationary source are removed from the gas stream using a heated (121°C or higher depending on stream conditions) glass probe. The gas is then passed through a heated line to the impinger system (see Figure 01-01-01-04A). Three of the midget impingers are filled with 15 ml of ICl and the fourth with silica gel. The ICl oxidizes any Hg present in the gas stream to Hg⁺², effectively scrubbing the Hg vapor. The gas stream is sampled for a minimum of 1.5 hours and 0.1 m³. The Hg content of the impingers is measured by flameless AAS back in the laboratory (see 02-02-01-02).	
Figure 01-01-01-04A. Hg Sampling Train.	
4. APPLICATION: Compliance, engineering evaluation R&D.	
A) OPERATIONAL SCOPE This method is applicable for the determination of mercury gaseous emissions from stationary sources. These test procedures are primarily used for determining compliance with clean air acts.	
B) INTERFERENCES/LIMITATIONS ICl has a large molecular background and can interfere with the AAS analysis. Method cannot be used in presence of easily oxidized background, e.g., SO₂.	
C) RECOMMENDED USE AREA Compliance Testing.	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.1 ppm mercury can be found in the impingers. B) ACCURACY N/Q (±10%). C) PRECISION N/Q (±10%).	
6. REAGENTS REQUIRED Potassium iodide, hydrochloric acid, potassium iodate, distilled water, iodine chloride, nitric acid, sodium hydroxide, zero grade air, mercuric chloride.	7. EQUIPMENT REQUIRED Sampling train (see Figure 01-01-01-04) barometer, anemometer, thermometer, laboratory glassware.
8. KEYWORD INDEX: Sampling, mercury sampling, compliance testing.	
9. CROSS REFERENCE ID NUMBERS 02-02-01-02.	
10. REFERENCES	
A) PRIMARY SOURCE 019 Federal Register, Vol. 36, No. 234, p. 23248, 1971.	
B) BACKGROUND INFORMATION 020 Martin, R.M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, APT-0581. 021 Smith, W.S., et al., "Stack Gas Sampling Improved and Simplified with New Equipment," APCA paper No. 67-119, 1967. 022 Hatch, W.R., and W.L. Ott, "Determination of Submicrogram Quantities of Mercury by Atomic Absorption Spectrophotometry," <i>Anal. Chem.</i> , 40, 2085 (1968). 023 Rome, J.J., "Maintenance Calibration and Operation of Isokinetic Source Sampling Equipment," EPA, APTD E-05-76. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Book of ASTM Standards, Part 23, D2928-71, "Standard Method for Sampling Stacks for Particulate Matter," American Society for Testing and Materials, Philadelphia, PA., 1971.	
C) FIELD APPLICATIONS	

1. TITLE SAMPLING VAPOROUS TRACE ELEMENTS IN FLUE GAS	2. IDENTIFICATION CODE 01-01-01-05
3. ABSTRACT OF METHODOLOGY	
A system of four impingers commonly found in a Method 5 train is filled with 3M H_2O_2 in the first impinger, 0.2 M $(NH_4)_2 S_2O_8$ plus 0.02 M $AgNO_3$ in the next two impingers, and Drierite in the last impinger. For the most accurate results, the Trace Material Sampling Train (01-04-01-01) is recommended. The 3M H_2O_2 passes Hg vapor but removes the SO_2 to prevent depletion of the Ag catalyzed $(NH_4)_2 S_2O_8$ solution. The persulfate solution is specifically designed to remove Hg, but will collect any Se, Sb, As or Pb that passes through the peroxide impinger. In all cases, the volatile species are oxidized in the H_2O_2 or $(NH_4)_2 S_2O_8$ and are effectively scrubbed from the gas stream.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE This oxidative system was designed to operate in the modified Aerotherm HVSS, but can be used in any commercially available system employing glass or plastic impingers. The system is 100% efficient for Hg scrubbing at flowrates up to 5 cfm. B) INTERFERENCES/LIMITATIONS $(NH_4)_2 S_2O_8$ is not stable in solution, so the solution must be made up just prior to use. Because of its strong oxidative nature, metal parts in contact with the solution will contaminate the sample with Ni, Cr, and Fe. Glass or plastic impingers are recommended. C) RECOMMENDED USE AREA Engineering evaluation of the gas streams for volatile trace metals.	
5. OPERATIONAL PARAMETERS	
A) RANGE Designed to sample trace quantities of Hg, Se, Sb, As and Pb in flue gas. B) ACCURACY System is 100% effective for Hg removal up to 5 cfm. C) PRECISION ($\pm 10\%$ estimated)	
6. REAGENTS REQUIRED $(NH_4)_2 S_2O_8$, H_2O_2 , high purity H_2O .	7. EQUIPMENT REQUIRED Glass or plastic impingers (Greenberg-Smith), pump, flowmeter (see 01-04-01-01).
8. KEYWORD INDEX: Sampling, vapors, Hg, Se, Sb, As, Pb.	
9. CROSS REFERENCE ID NUMBERS 01-04-01-01; 02-01-03-03.	
10. REFERENCES	
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements of Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975. B) BACKGROUND INFORMATION C) FIELD APPLICATIONS 025 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Final Report for Measurements Techniques for Inorganic Trace Materials in Control System Streams," TRW Defense and Space Systems, EPA Contract Number 68-02-1393, in press.	

1. TITLE DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES	2. IDENTIFICATION CODE 01-01-01-06
3. ABSTRACT OF METHODOLOGY A gas sample is removed from a sampling point in the stack and collected in a series of impingers, as shown in Figure 01-01-01-06A. The sulfuric acid mist, including SO ₃ , is collected both in the first impinger containing 80% isopropanol, and on the filter. The SO ₂ is collected in the second and third impingers, which contain 3% hydrogen peroxide solution. The four impingers are Greenburg-Smith impingers. The first and third impingers have standard tips; the second and fourth impingers are modified by replacing the standard tip with a 1/2-inch ID glass tube extending to one-half inch from the bottom of the impinger flask. Analysis on the sampled gases are performed using the barium-thorin titration method (see 02-03-02-05).	
Figure 01-01-01-06A. Sulfuric Acid Mist Sampling Train	
4. APPLICATION: Compliance.	
A) OPERATIONAL SCOPE Method is applicable to determination of sulfuric acid mist (including SO ₃) and SO ₂ from stationary sources when specified by test procedures for new source performance standards.	
B) INTERFERENCES/LIMITATIONS SO ₂ may be trapped in the isopropyl alcohol solution, causing low results. The alcohol solution should be purged with nitrogen into the hydrogen peroxide impingers to remove any SO ₂ trapped in the IPA. At recommended temperatures H ₂ SO ₄ will condense in the probe and tubing leading to the first impinger.	
C) RECOMMENDED USE AREA	
5. OPERATIONAL PARAMETERS	
A) RANGE N/Q B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED Glass fiber filters, silica gel, 80% isopropanol, 3% hydrogen peroxide, crushed ice.	7. EQUIPMENT REQUIRED Sampling probe, nozzle, pitot tube, filter holder, metering system, barometer, impingers, standard laboratory glassware.
8. KEYWORD INDEX: Flue gas sampling, sulfuric acid mist, sulfur dioxide, compliance.	
9. CROSS REFERENCE ID NUMBERS 01-01-01-01; 02-03-02-05.	
10. REFERENCES	
A) PRIMARY SOURCE 006 Federal Register, "Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources," 36 (247), 24893 (1971).	
B) BACKGROUND INFORMATION 007 U.S. DHEW, PHS Division of Air Pollution, "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes," PHS Publication NO. 999-AP-13, Cincinnati, Ohio, 1965. 008 Patton, W.F., and J.A. Brink, Jr., "New Equipment and Techniques for Sampling Chemical Process Gases," J.A.P.C.A., 8, 162 (1963). 565 "Collaborative Study of Method for the Determination of H ₂ SO ₄ Mist and SO ₂ Emissions from Stationary Sources," EPA-650/4-75-003, Nov. 1974.	
C) FIELD APPLICATIONS 009 Corbett, D.F., "The Determination of SO ₂ and SO ₃ in Flue Gases," J. Inst. Fuel, 24, 217-243 (1961). 482 Rom, J.J., "Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0576.	

1. TITLE DETERMINATION OF HYDROGEN SULFIDE EMISSIONS FROM STATIONARY SOURCES	2. IDENTIFICATION CODE 01-01-01-07
3. ABSTRACT OF METHODOLOGY A sample of gas is removed from the gas stream and hydrogen sulfide is collected in a series of midget impingers containing alkaline cadmium hydroxide (see Figure 01-01-01-07A). The cadmium sulfide which precipitates is then dissolved in hydrochloric acid solution and absorbed in iodine, then is titrated with standard thiosulfate solution (see 02-03-02-17).	
Figure 01-01-01-07A. Field Data	
4. APPLICATION: Compliance.	
A) OPERATIONAL SCOPE Method is applicable to measurement of H_2S to determine compliance with New Source Performance Standards.	
B) INTERFERENCES/LIMITATIONS The analysis titration should be conducted at the sampling location in order to prevent iodine loss from the sample. The sample should not be exposed to direct sunlight during titration.	
C) RECOMMENDED USE AREA	
5. OPERATIONAL PARAMETERS	
A) RANGE N/Q B) ACCURACY N/Q C) PRECISION N/Q	
6. REAGENTS REQUIRED Cadmium sulfate hydrate, sodium hydroxide, 3% hydrogen peroxide, hydrochloric acid solution, ice.	7. EQUIPMENT REQUIRED Sampling probe, impingers, silica gel drying tube, standard laboratory glassware.
8. KEYWORD INDEX: Flue gas sampling, H_2S , compliance, sampling.	
9. CROSS REFERENCE ID NUMBERS 02-03-02-17; 01-02-01; 01-02-02	
10. REFERENCES	
A) PRIMARY SOURCE 481 U.S. Environmental Protection Agency, "Determination of Hydrogen Sulfide Emissions from Stationary Sources," Title 40, Part 60, Chapter 1, Appendix A, Washington, D.C., 1971, p. 792.	
B) BACKGROUND INFORMATION 483 "Determination of Hydrogen Sulfide, Ammoniacal Cadmium Chloride Method," API Method 772-54, in "Manual on Disposal of Refinery Wastes," Volume 5, American Petroleum Institute, Washington, D.C., 1954. 484 "Tentative Method for Determination of Hydrogen Sulfide and Mercaptan Sulfur in Natural Gas," Natural Gas Processors Association, Tulsa, Oklahoma, NGPA Publication No. 2265-65, 1965.	
C) FIELD APPLICATIONS	

1. TITLE SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES		2. IDENTIFICATION CODE 01-01-01-08
3. ABSTRACT OF METHODOLOGY		
Method involves the measurement of the distance from the chosen sampling location to the nearest upstream and downstream disturbances. The sampling site should be at least eight stack- or duct-diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, contraction, or flame. The minimum number of traverse points is then 12. The equivalent diameter of a rectangular cross section is determined using Equation (1): $\text{equivalent diameter} = 2 \left(\frac{(\text{length})(\text{width})}{\text{length} + \text{width}} \right) \quad (1)$ When the above criteria cannot be met, the number of sampling points for each distance is selected from Figure 01-01-01-08A. Next, the cross-sectional layout and location of traverse points are determined. Traverse points for circular stacks are located using Figure 01-01-01-08B and Table 01-01-01-08A. Traverse points for rectangular stacks are located using Figure 01-01-01-08C.		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to the measurement of gas streams emitted to the atmosphere without further processing, to determine compliance with New Source Performance Standards. B) INTERFERENCES/LIMITATIONS N/Q C) RECOMMENDED USE AREA This is the compliance method for the positioning of velocity and sampling traverses.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method can be used to sample all gaseous streams. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
None.	Linear measurement equipment.	
8. KEYWORD INDEX: Sample traverse, velocity traverse, flue gas, compliance.		
9. CROSS REFERENCE ID NUMBERS 02-02; 02-03; 01-01-01-09		
10. REFERENCES		
A) PRIMARY SOURCE 481 U.S. Environmental Protection Agency, "Sample and Velocity Traverse for Stationary Sources," Title 40, Part 60, Chapter 1, Appendix A, Washington, D.C., 1971, p. 760. B) BACKGROUND INFORMATION 485 "Determining Dust Concentration in a Gas Stream," ASME Performance Test Code #27, New York, N.Y., 1957. 486 Devorkin, H., et al, "Air Pollution Source Testing Manual," Air Pollution Control District, Los Angeles, California, Nov. 1963. 487 "Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases," Western Precipitation Division of Joy Manufacturing Co., Los Angeles California, Bulletin WP-50, 1968. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, 02928-71, "Standard Method for Sampling Stacks for Particulate Matter," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 832-858. C) FIELD APPLICATIONS		

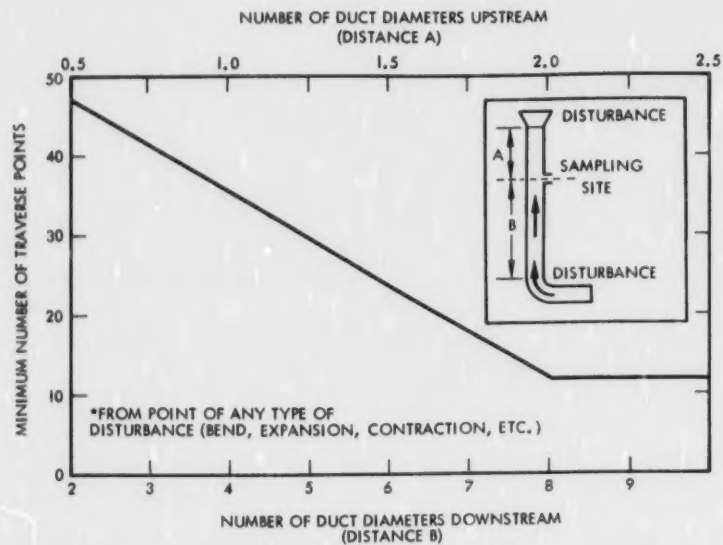


Figure 01-01-01-08A. Minimum Number of Traverse Points



Figure 01-01-01-08B. Cross Section of Circular Stack Divided into 12 Equal Areas, Showing Location of Traverse Points at Centroid of each Area

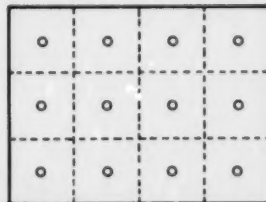


Figure 01-01-01-08C. Cross Section of Rectangular Stack Divided into 12 Equal Areas, with Traverse Points at Centroid of Each Area

TITLE SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES (CONTINUED)

ID NO. 01-01-01-00

FIGURE 01-01-01-00C.
 LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS
 (Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	35.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	63.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	92.3	88.4	83.9
19										95.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

1. TITLE STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)		2. IDENTIFICATION CODE 01-01-01-00
3. ABSTRACT OF METHODOLOGY		
Method involves determination of stack gas velocity using gas density and velocity head measurement using a Type S (Stauscheibe or reverse type) pitot tube. Figure 01-01-01-09 shows the pitot tube-monometer assembly. The stack velocity head and temperature are measured at traverse points specified in 01-01-01-08. Next, static pressure is measured. Finally, stack gas molecular weight is determined by gas analysis and calculations (see Method 02-03-01-01). Excess air is calculated using Equation 1: $\% EA = \frac{(\% O_2) - 0.5(\% CO)}{0.264(\% N_2) - (\% O_2) + 0.5(\% CO)} \times 100 \quad (1)$ and dry molecular weight is calculated using Equation 2: $M_d = 0.44(\% CO_2) + 0.32(\% O_2) + 0.28(\% N_2 + \% CO) \quad (2)$		
4. APPLICATION: Compliance		
A) OPERATIONAL SCOPE Method is applicable to the measurement of stack gas streams to determine compliance with new Source Performance Standards. B) INTERFERENCES/LIMITATIONS S-pitot tubes are very susceptible to misalignment in the gas flow for accurate measurements. be sure to align s-pitot parallel to gas flow. C) RECOMMENDED USE AREA This is the compliance method for performing velocity traverses.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method can be used to measure all gaseous streams. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
None.		Pitot tube - Type S, differential pressure gauge, temperature gauge, pressure gauge, barometer, gas analyzer.
8. KEYWORD INDEX: Stack gas velocity, volumetric flow rate, compliance		
9. CROSS REFERENCE ID NUMBERS 02-02; 02-03; 01-01-01-08		
10. REFERENCES		
A) PRIMARY SOURCE 481 U.S. Environmental Protection Agency, "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)," Title 40, Part 60, Chapter 1, Appendix A, Washington, D. C., 1971, p. 763. B) BACKGROUND INFORMATION 488 Mark, L.S., "Mechanical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York, N.Y., 1951. 489 Perry, J.H., "Chemical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York, N.Y., 1960. 490 Shighara, R.T., W.S. Smith, and W.F. Todd, "Significance of Errors in Stack Sampling Measurements," paper presented at the annual meeting of the Air Pollution Control Association, St. Louis, MO., June 14-19, 1970. 491 Vennard, J.K., "Elementary Fluid Mechanics," John Wiley and Sons, Inc., New York, N.Y., 1947. C) FIELD APPLICATIONS		

TITLE STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE
(TYPE S PITOT TUBE) (CONTINUED)

ID NO. 01-01-01-08

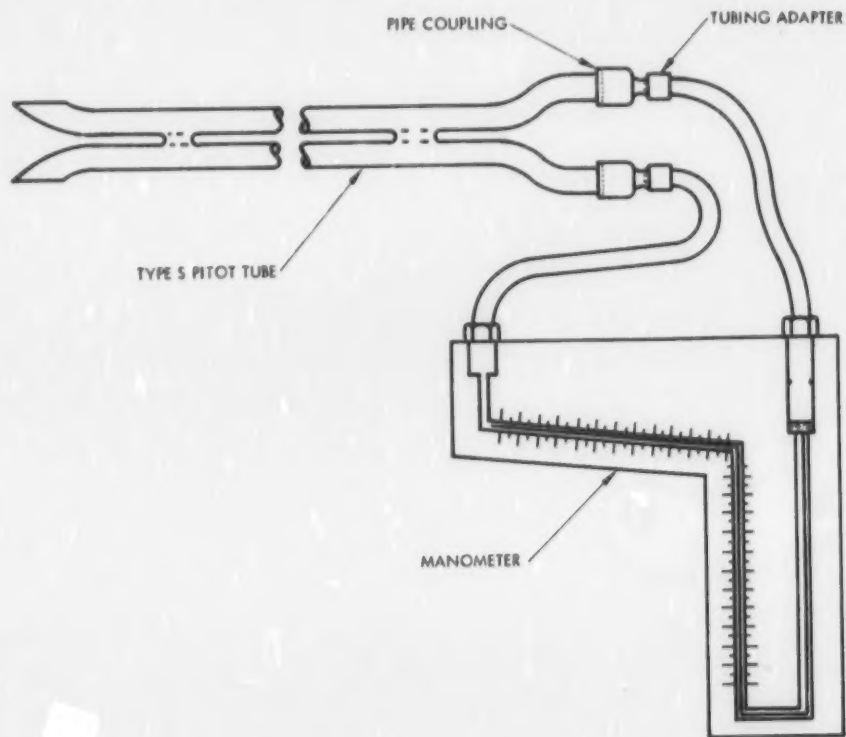


Figure 01-01-01-09. Pitot Tubemanometer Assembly

2. IDENTIFICATION CODE

01-01-02-01

1. TITLE SAMPLING FLUE GASES USING DIRECT READING GAS DETECTION TUBES**3. ABSTRACT OF METHODOLOGY**

Gas detection tubes are based on the principle that if a known volume of gas containing a species of interest is pulled through a tube that contains a solid adsorbent impregnated with an indicating reagent, that the length of the stain on the indicating gel will be proportional to the amount of gas species in the sampled air. The use of detecting tubes is extremely simple. After their two sealed ends are broken open, the glass tubes are placed in the manufacturer's holder which is fitted with a calibrated squeeze bulb or piston pump. The recommended air volume is then drawn through the tube by the operator. When sampling hot gases, such as from a furnace stack or an exhaust, cooling of the sample gas is essential, otherwise the calibration would be inaccurate and the volume of gas sampled uncertain. A probe of glass or metal may be attached to the inlet end of the detector tube with a short piece of flexible tubing. If this tube is cold initially, a length of as little as 10.2 cm (4 inches) outside of the furnace is sufficient to cool the gas sample from 250°C to about 30°C. Note: One must be careful in employing this type of probe since in some cases serious adsorption (for example SO₂) errors can occur either on the tube or in condensed moisture.

4. APPLICATION: Environmental assessment.**A) OPERATIONAL SCOPE**

By using a probe to cool the gas prior to sampling with the detection tube, the temperature range under which the detection tube can be used can be extended to as high as 572°C. Since precleansing layers are present in the detection tube, the interferences to the specific measurement are minimized. These tubes can be used to sample most flue gases as long as the pressure in the stack is close to ambient. Instructions are provided with the tube to correct for temperature and pressure changes.

B) INTERFERENCES/LIMITATIONS

Even with the precleansing layers there are interferences to the gases being measured (see Table 01-01-02-01A). One must always be aware of possibility of spurious results because of these interferences. Experience in sampling a known concentration is of great value in training the operator to know whether to measure the length of the beginning or end of the stained front or what portion of the original shaped stain to use as the limit. Care must be taken to see that the pump valves and connections are leak-proof. The color in the indicating tube can fade with time, so the measurement of the stain length should be accomplished as soon as possible. If the tube is to be kept as evidence, then both ends should be sealed with wax.

C) RECOMMENDED USE AREA

Level 1 environmental assessment.

5. OPERATIONAL PARAMETERS See Table 01-01-02-01A.**A) RANGE** N/Q**B) ACCURACY** The tube reading deviates from the true value by $\pm 25\%$ at most. For many tubes, the deviation is less than $\pm 10\%$.**C) PRECISION** Precision will primarily depend upon the technique of the operator in measuring the length of the stain.**6. REAGENTS REQUIRED**

Detector tubes can be obtained from several sources. (National Mines Service Co., Pittsburgh, Pa., and Unico Environmental Instruments, Fall River, Mass.)

7. EQUIPMENT REQUIRED

A gas detection kit normally includes detection tubes of interest and necessary pumps and attachments needed to perform the test.

8. KEYWORD INDEX: Sampling, detection tubes.**9. CROSS REFERENCE ID NUMBERS** 01-01-02-01.**10. REFERENCES****A) PRIMARY SOURCE**

026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments," ACGIH, Cincinnati, Ohio, 4th ed., 1972, p. S-1 to S-50.

B) BACKGROUND INFORMATION

See Table 01-01-02-01B.

C) FIELD APPLICATIONS

See Table 01-01-02-01C.

TITLE SAMPLING FLUE GASES USING DIRECT READING GAS DETECTION
TUBES (CONTINUED)

ID NO. 01-01-02-01

Table 01-01-02-01A. UNICO (KITAGAMA) Gas Detector Tubes (Reference 026).

Detector Tube	Measurable Concentration	T.L.V.	Lower Explosive Limit	Shelf Life	Discoloring of Reagent Original Change		Interferences
Ammonia-high range	1-25%	0.005%	15%	unlimited	pink	purplish blue	Hydrogen sulfide
Ammonia-low range	20-700 PPM	50 PPM	160,000 PPM	1 year†	pink	pale yellow	Amines
Arsine	5-160 PPM	0.05 PPM	—	3 years	white	brownish black	Hydrogen sulfide, phosphine
Bromine	10-300 PPM	0.1 PPM	—	1 year†	white	greenish orange	Chlorine, iodine, nitrogen dioxide
Carbon Dioxide-high range	0.1-2.6%	0.5%	—	3 years	blue purple	pale pink	Acid gases at high concentration
Carbon Dioxide-low range	300-7,000 PPM	5,000 PPM	—	3 years	blue purple	pale pink	Acid gases at high concentration
Carbon Disulfide	10-200 PPM	20 PPM	12,500 PPM	1 year†	blue purple	white	Hydrogen sulfide above 50 PPM, sulfur dioxide above 150 PPM
Carbon Monoxide	25-6,000 PPM	50 PPM**	125,000 PPM	3 years	pale yellow	green and blue	Hydrocarbons, hydrogen sulfide, nitrogen dioxide, ammonia
Carbon Monoxide—in the presence of ethylene	25-6,000 PPM	50 PPM**	125,000 PPM	3 years	pale yellow	green and blue	Nitrogen dioxide
Carbon Monoxide—in the presence of hydrocarbons and nitrous gases	25-6,000 PPM	50 PPM**	125,000 PPM	1 year†	pale yellow	green and blue	none
Carbon Tetrachloride	5-300 PPM	10 PPM	—	6 months†	yellow	blue	Phosgene
Chlorine	1-40 PPM	1 PPM**	—	1 year†	white	pale orange	Other halogens, ozone, nitrous gases, bromine, iodine
Chlorine Dioxide	10-500 PPM	0.1 PPM	—	1 year†	white	orange	Chlorine, ozone, nitrous gases, iodine
Hydrogen Cyanide-high range	0.01-3.0%	0.001%	6%	1 year†	yellow	reddish brown	Cyanogen, hydrogen sulfide, sulfur dioxide
Hydrogen Cyanide-low range	10-100 PPM	10 PPM	—	1 year†	yellow	red	Hydrogen chloride, sulfur dioxide
Hydrogen Selenide	1-600 PPM	0.05 PPM	—	1 year†	pale yellow	dark brown	Arsine, hydrogen sulfide
Hydrogen Sulfide-high range	0.01-0.17%	0.001%**	4.3%	3 years	white	black	Sulfur dioxide
Hydrogen Sulfide-low range	5-160 PPM	10 PPM**	43,000 PPM	1 year†	white	brown	Sulfur dioxide
Hydrogen Sulfide—in the presence of sulfur dioxide	0.005-0.16%	0.001%**	4.3%	3 years	pale yellow	blackish blue	Hydrocarbons, carbon monoxide, nitrous gases, hydrogen cyanide
Hydrogen Sulfide	1000-3000 PPM	10 PPM**	—	3 years	white	black	Sulfur dioxide
Mercury (inorganic)	0.1-2.0 mg/m ³	0.1 mg/m ³	—	1 year†	yellowish gray	pale orange	Chlorine, hydrogen sulfide
Methyl Mercaptan	1-20 PPM 5-120 PPM	10 PPM**	—	1 year†	white	orange	Methyl sulfide, chlorine, acetylene, nitrogen dioxide, carbon monoxide, ethylene, ethyl mercaptan
Nickel Carbonyl	20-700 PPM	0.001 PPM	—	6 mos.†	pale yellow	blackish purple	Hydrogen sulfide, sulfur dioxide
Nitrogen Dioxide	1-1,000 PPM	5 PPM	—	1 year†	grayish white	pale orange	Chlorine, ozone, iodine, bromine, chlorine dioxide
Oxygen	2-30%	—	—	1 year†	white	brown	none
Phosgene	5-50 PPM	0.1 PPM**	—	1 year†	white	reddish brown	Chlorine, nitrogen dioxide, hydrogen chloride

** Tentative — 1967 Revision † All short shelf life tubes can be extended by refrigeration.

**TITLE SAMPLING FLUE GASES USING DIRECT READING GAS DETECTION
TUBES (CONTINUED)**

ID NO. 01-01-02-01

Table 01-01-02-01A. UNICO (KITAGAWA) Gas Detector Tubes (Continued)

Detector Tube	Measurable Concentration	T.L.V.	Lower Explosive Limit	Shelf Life	Discoloring of Reagent Original	Change	Interferences
Phosphine-high range	20-800 PPM	0.3 PPM	-	unlimited	pale blue	reddish purple	Hydrogen sulfide
Phosphine-low range	5-90 PPM	0.3 PPM	-	unlimited	pale blue	yellowish brown	Hydrogen sulfide
Sulfur Dioxide-high range	0.1-0.4%	0.0005%	-	unlimited	yellow	light blue	Hydrogen sulfide
Sulfur Dioxide-middle range	0.02-0.3%	0.0005%	-	3 years	white	orange	Hydrogen sulfide
Sulfur Dioxide-low range	5-300 PPM	5 PPM	-	1 year+	blue purple	white	Hydrogen sulfide
Sulfur Dioxide-D type	1-80 PPM	5 PPM	-	1 year+	blue purple	white	Hydrogen sulfide, nitrogen dioxide
Sulfur Dioxide-determinations in flue gases	0.02-0.30%	5 PPM	-	3 years	white	orange	none

+All short shelf life tubes can be extended by refrigeration.

Table 01-01-02-01B Background Information

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- 028 Hubbard, B.R., and L. Silverman, *Arch. Ind. Hyg. and Occ. Med.*, 2, 49 (1950).
- 029 Grosskopf, Karl, *Agnew, Chem.*, 63, 306 (1951).
- 030 Grosskopf, Karl, "Detector Tubes as Detectors in Gas Chromatography," (German) *Erdohl und Kohle*, 11, 304-6 (1958).
- 031 Ingram, W.T., "Personal Air-Pollution Monitoring Devices," *Am. Ind. Hyg. Assoc. J.*, 25, 298-303 (1964).
- 032 Kinoshita, J.R., and B.R. Hubbard, "Nitrogen Dioxide Indicator," *Amer. Ind. Hyg. Assoc. J.*, 19, 453 (1958).
- 033 Kitagawa, Tetsuzo, "Rapid Method of Quantitative Gas-Analysis by Means of Detector Tubes," *Kagaku no Ruotki*, 6, 386 (1952).
- 034 Sacks, Volkmar, "Carbon Monoxide Detection by Means of the Colorimetric Gas Analyzer," (German) *Deutsche Zeitschrift Fur Gerichtliche Medizin*, 45, 68-71 (1956).
- 035 Silverman, Leslie, and G.R. Gardner, "Potassium Pallado Sulfite Method for Carbon Monoxide Detection," *Am. Ind. Hyg. Assoc. J.*, 26, 97-105 (1965).
- 036 Kusnetz, H.L., "Air Flow Calibration of Direct Reading Colorimetric Gas Detecting Devices," *Amer. Ind. Hyg. Assoc. J.*, 21, 340-1 (1960).
- 037 Saltzman, Bernard E., "Basic Theory of Gas Indicator Tube Calibrations," *Am. Ind. Hyg. Assoc. J.*, 23, 112-26 (1962).
- 038 Scherberger, R.F., D.W. Fassett, G.P. Hapo and F.A. Miller, "A Dynamic Apparatus for Preparing Air-Vapor Mixtures of Known Concentrations," *Am. Ind. Hyg. Assoc. J.*, 19, 494-8 (1958).
- 039 Saltzman, Bernard E., "Preparation and Analysis of Calibrated Low Concentrations of Sixteen Toxic Gases," *Anal. Chem.*, 33, 1100-12 (1961).
- 040 Cotabish, H.N., P.W. McConaughy and H.C. Messer, "Making Known Concentrations for Instrument Calibration," *Am. Ind. Hyg. Assoc. J.*, 22, 392-402 (1961).
- 041 Hersch, P.A., "Controlled Addition of Experimental Pollutants to Air," *J. Air Poll. Control Assoc.*, 19, 164-72 (1969).
- 042 Kusnetz, H.L., M.E. Lanier and B.E. Saltzman, "Calibration and Evaluation of Gas Detecting Tubes," *Am. Ind. Hyg. Assoc. J.*, 21, 361-73 (1960).

Table 01-01-02-01C Field Applications

- 043 Ketcham, N.H., "Practical Experiences with Routine Use of Field Indicators," *Am. Ind. Hyg. Assoc. J.*, 23, 127-31 (1962).
- 044 Kitagawa, Tetsuzo, "Detection of Underground Spontaneous Combustion in Its Early Stage With Detector," Tenth International Conference of Directors of Safety in Mines Research, Pittsburgh, Pennsylvania, 1959.
- 045 Kitagawa, Tetsuzo, "The Rapid Measurement of Toxic Gases and Vapors," The 13th International Congress on Occupational Health, New York, N.Y., July 25-9, 1960.
- 046 Silverman, L., "Panel Discussion of Field Indicators in Industrial Hygiene," *Am. Ind. Hyg. Assoc. J.*, 23, 108-11 (1962).
- 047 Silverman, Leslie, "Techniques to Improve the Accuracy of Detector Tubes," *Am. Ind. Hyg. Assoc.*, Cincinnati, Ohio, May 1963.
- 048 Banks, O.M., and D.R. Nelson, "Evaluation of Commercial Detector Tubes," presented at 22nd Annual Meeting, *Am. Ind. Hyg. Assoc.*, Detroit, Michigan, April 13, 1961.
- 049 Hay III, E.B., "Exposure to Aromatic Hydrocarbons in a Coke Oven By-Product Plant," *Am. Ind. Hyg. Assoc. J.*, 25, 386-91 (1964).
- 050 Lanier, M.B., and H.L. Kusnetz, "Practices in the Field Use of Detector Tubes," *Arch. Environmental Health*, 6, 418-21 (1963).
- 051 Kitagawa, Tetsuzo, "Detector Tube Method for Rapid Determination of Minute Amounts of Nitrogen Dioxide in the Atmosphere," Yokohama National Univ. (July 1965).

1. TITLE SO ₂ ADSORPTION ON SOLIDS (SILICA GEL)		2. IDENTIFICATION CODE 01-01-02-02
3. ABSTRACT OF METHODOLOGY		
Figure 01-01-02-02A shows a typical sampling apparatus for SO₂ adsorption. The tube is placed in an appropriate sample port. A known volume of flue gas is drawn through the tube using an evacuated cylinder of known volume or a metered pump. The adsorbed SO₂ is desorbed at 500°C, then reduced in a hydrogen stream to H₂S, which is then determined spectrophotometrically as molybdenum blue. A typical desorption apparatus consists of a hydrogen source (steel cylinder and laboratory gas meter), a furnace, a quartz contact tube (26 cm x 8 mm I.D.) containing 3 x 6 cm² platinum wire grid of 3600 mesh/cm², connected to a reagent scrubber containing 5 ml reagent solution. Desorption consists in heating the silica gel tube in the presence of the hydrogen gas to 500°C; the desorbed gas is then passed over the platinum catalyst and heated in the presence of hydrogen to 600°C by the contact burner. The H₂S which is formed is then allowed to pass through a tube containing 5 ml of reagent solution (see Section 6 below for reagent composition). The resulting solution is analyzed spectrophotometrically, as indicated above. Other general methods for desorbing gases and vapors from silica gel include blowing with contaminant-free air at temperatures up to 350°C, extraction with polar solvents such as water or alcohols, and distillation with saturated steam at ambient pressures (see 01-05-02-04). Silica gel can also be used as an adsorbent for H₂S, NH₃ and AsH₃, if impregnated with suitable reagents prior to sampling. Impregnants include solutions of lead acetate or silver cyanide for hydrogen sulfide, sulfuric acid for NH₃, and copper and silver oxidation catalysts for arsine.		
4. APPLICATION: Environmental assessment, engineering evaluation R&D		
A) OPERATIONAL SCOPE The method is applicable to sampling most flue gas streams containing SO₂, involving temperatures of 200°C, and pressures of 1 atmosphere. B) INTERFERENCES/LIMITATIONS Trace sulfur-containing contaminants must be removed from the silica prior to use as an adsorbent by heating several hours in nitric acid in a water bath under a reflux condenser. C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment method for sampling flue gases containing SO₂.		
5. OPERATIONAL PARAMETERS		
A) RANGE Sampling rate of 2 to 10 m³ of stack gas over period of 1 to 4 hours (See 01-01-01-04) is possible. The range sensitivity of the method can be increased by impregnation with suitable solutions, as described above. B) ACCURACY 10% or better. C) PRECISION ±10% or better.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Purified silica gel; reagent solution, consisting of 2 volumes of A + 3 volumes of B (A = 0.5g urea in 1000 ml 1 N H ₂ SO ₄ ; B = 33.3g ammonium molybdate in 1000 ml water); solutions for impregnating silica gel (lead acetate, silver cyanide, sulfuric acid).	Adsorption tube; desorption apparatus including quartz contact tube (length, 26 cm; 8 mm I.D.) containing tightly coiled 3 x 6 cm ² platinum wire grid of 3600 mesh/cm ² ; furnace, steel cylinder of hydrogen and laboratory gas meter.	
8. KEYWORD INDEX: Adsorption on solids, SO ₂ , silica gel, desorption.		
9. CROSS REFERENCE ID NUMBERS 01-05-02-04, 01-05-04-01; 01-01-04-01, 01-01-02-03; 02-03-01; 01-01-01-04.		
10. REFERENCES		
A) PRIMARY SOURCE 052 Leithe, W., "The Analysis of Air Pollution," London, Ann Arbor-Humphrey Science Publishers, 1970, p. 158-60. B) BACKGROUND INFORMATION 026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments for Evaluation of Atmospheric Contaminants," Cincinnati, Ohio, 4th ed., 1972, p. R-5 and R-6. C) FIELD APPLICATIONS		

TITLE SO₂ ADSORPTION ON SOLIDS (SILICA GEL) (CONTINUED)

ID NO. 01-01-02-02

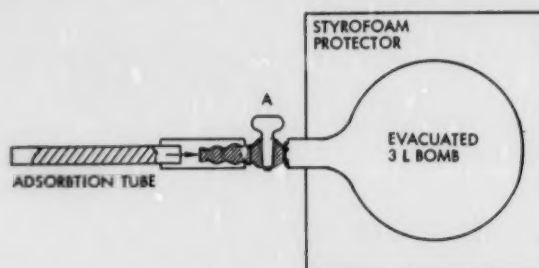


Figure C1-01-02-02A. Evacuated Grab Sampling Apparatus (3 liters).

1. TITLE SULFUR OXIDES IN FLUE GAS BY CONTROLLED CONDENSATION (GOKSOYR-ROSS METHOD)	2. IDENTIFICATION CODE 01-01-03-01
3. ABSTRACT OF METHODOLOGY Using a borosilicate glass probe of suitable length, gas samples are removed from the stack. Particulates are removed from the gas stream by a quartz wool plug placed at the end of the heated (250°C) probe. The sulfur trioxide is condensed as sulfuric acid by controlled cooling of the flue gas as it passes through a water jacketed (62°C) condenser. The resulting sulfuric acid aerosol is collected on a filter which is maintained above the water dewpoint by the water jacket to prevent SO ₂ from being washed out of the gas stream. Sulfur dioxide is collected in midget impingers in a series with the SO ₂ collector and oxidized to sulfuric acid by aqueous 3 percent hydrogen peroxide solution. The sulfate concentration of each solution is then determined separately (see 02-03-02-03 for details of a sulfate procedure recommended for this sampling method).	
Figure 01-01-03-01A. Goksoyr/Ross Coil (Reference 053).	
4. APPLICATION: Engineering evaluation R&D, environmental assessment.	
A) OPERATIONAL SCOPE This method covers the high precision determination of sulfur oxide emissions in flue gases.	
B) INTERFERENCES/LIMITATIONS It is also possible that SO ₂ can be oxidized by the quartz wool or by the particulates collected on the quartz wool. The temperature of the particulate filter should be kept >225°C.	
C) RECOMMENDED USE AREA Engineering evaluation R&D of flue gas streams for SO ₃ .	
5. OPERATIONAL PARAMETERS	
A) RANGE This method is applicable to the determination of SO ₂ from 10 - 3000 ppm and SO ₃ from 10 - 300 ppm.	
B) ACCURACY 5% (estimated).	
C) PRECISION For SO ₂ , ±2.6% at 1500 ppm. For SO ₃ , ±5% at 10 ppm (estimated).	
6. REAGENTS REQUIRED Ethyl alcohol, hydrogen peroxide, high purity water.	7. EQUIPMENT REQUIRED Borosilicate glass, probe with heating attachment, SO ₃ condenser coil (see Figure 01-01-03-01A), midget impingers, critical orifice meter, powerstats, stop watch, thermometer, plastic bottles, laboratory glassware, constant water bath.
8. KEYWORD INDEX: Sampling, sulfur trioxide, sampling.	
9. CROSS REFERENCE ID NUMBERS 02-03-02-03.	
10. REFERENCES	
A) PRIMARY SOURCE 053 ASTM Standards, Part 26, "Tentative Method for Test for Sulfur Oxides in Flue Gases (Barium Chloranilate Controlled Condensation Method)," ASTM Method D3226-73T, 1974, p. 700.	
B) BACKGROUND INFORMATION 054 Goksoyr, H., and K. Ross, <i>Journal of Institute of Fuel</i> (London), 35 , 177 (1962). 055 Lisle, E.S., and J.D. Sensenbaugh, <i>Combustion</i> , 36 , 12 (1965). 056 Burger, A.W., J.N. Driscoll, and P. Morgenstern, <i>Ind. Hyg. Assoc. J.</i> , 33 , 3397 (1972).	
C) FIELD APPLICATIONS 012 Driscoll, J.N., and A.W. Berger, "Improved Chemical Methods for Sampling & Analysis of Gaseous Pollutants from Combustion of Fossil Fuels," Final Report, Vol. 1, Sulfur Oxide, Contract No. CPA22-69-95 (June 1971), APD No. 1106, p. 209.	

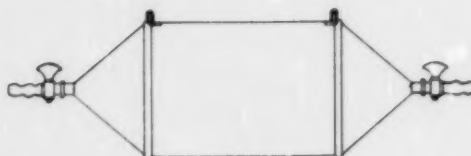
1. TITLE GENERAL GAS GRAB SAMPLING TECHNIQUES		2. IDENTIFICATION CODE 01-01-04-01
3. ABSTRACT OF METHODOLOGY		
When there is an abundant supply of gas, an air displacement procedure may be used to obtain a sample. The procedure involves purging the sample container (which is connected to an appropriate probe and line, and which precedes any impingers located in the sampling train) with a volume of gas equivalent to 10 times the sample container volume prior to collection of the sample. Typical glass and metal sample containers are shown in Figure 01-01-04-01A. If the gas is under low pressure, an aspirator or suction device is first connected to the end of the sample container for purging purposes. A liquid displacement method is used when the gas supply is limited. Composite continuous samples of several cubic feet or larger can also be taken using liquid displacement techniques. Figure 01-01-04-01B shows a gas grab purge sampling apparatus, including a simple open-end sampling probe.		
4. APPLICATION: Environmental assessment, engineering evaluation R&D.		
A) OPERATIONAL SCOPE Method is applicable to sampling flue gases and other streams involving temperatures of 200°C, and pressures slightly greater than 1 atm. B) INTERFERENCES/LIMITATIONS Gases containing corrosive constituents must be avoided, in order to prevent damage to lines, containers and auxiliary equipment. Interferences to sampling by air contamination, leakage, absorption/chemical reaction must be avoided. The successful application of the sampling method must reflect consideration of purpose for which sample is collected, in terms of volume of sample required, size and length of sampling line, and size and design of containers. C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment procedure for sampling inorganic gases, acid gases, and sulfur compounds.		
5. OPERATIONAL PARAMETERS		
A) RANGE Range is primarily governed by size and design of sample containers, and to a lesser extent, the other components of sampling equipment. Typical sampling rate is 2 to 10 m³ of gas over 1-to 4-hour period. B) ACCURACY N/Q C) PRECISION ±10%		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Mercury, or other liquid, for liquid displacement method.	Sampling probes, preferably metal sampling lines (iron pipe, copper, monel metal, brass tubing; glass or quartz tubing for sulfur compounds sampling at low pressures, aluminum tubing for sulfur compound sampling at high pressures). Sample containers (glass, steel, metal, or metal alloys) (see Figure 01-01-04-01A and B); aspirators and pumps; stopcock lubricant.	
8. KEYWORD INDEX: Gas sampling, grab, composite continuous sampling, air displacement, liquid displacement.		
9. CROSS REFERENCE ID NUMBERS 01-05-04-01; 01-01-01-04; 02-02-01; 02-03-01.		
10. REFERENCES		
A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels, Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D1247-54. 058 "Standard Method of Sampling Manufactured Gas," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 222-231. Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Process Measurements, Lurgi Coal Gasification Process," TRW Systems Group, EPA Contract No. 68-02-1412, March 1975, p. 5-4. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1605-60, "Sampling Atmospheres for Analysis of Gases and Vapors," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 349-370. 052 Leithe, W., "The Analysis of Air Pollutants," Ann Arbor-Humphrey Science Publishers, Ann-Arbor, Michigan, 1970. C) FIELD APPLICATIONS 058 Cropper, F.R., and S. Kaminsky, "Determination of Toxic Organic Compounds in Admixture in the Atmosphere by Gas Chromatography," <i>Anal. Chem.</i>, 35(6), 735 (1963). 059 Novak, J., J. Janak and V. Vasak, "Chromatographic Method for the Concentration of Trace Impurities in the Atmosphere and Other Gases," <i>Anal. Chem.</i>, 37(6), 660-666 (1965).		

TITLE GENERAL GAS GRAB SAMPLING TECHNIQUES (CONTINUED)

ID NO. 01-01-04-01



Type C



Type F

ASTM D 1247

Figure 01-01-04-01A. Glass and Metal Sample Containers (Reference 057).

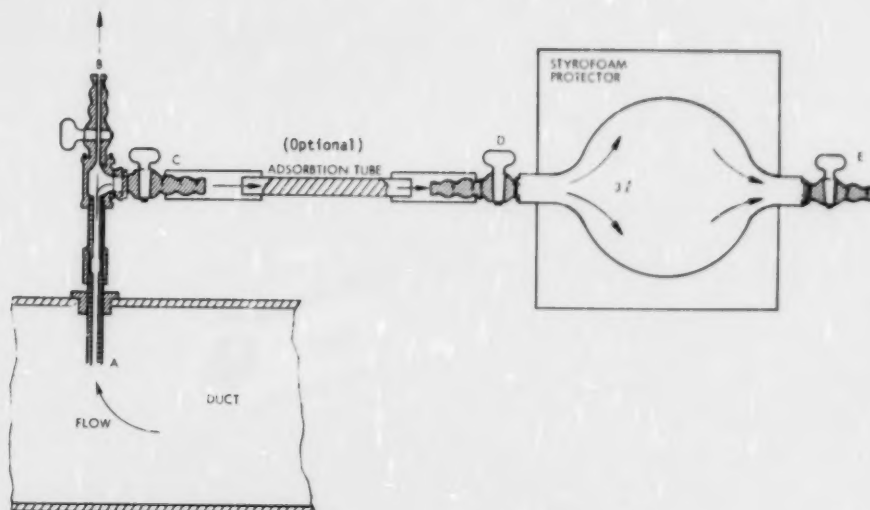


Figure 01-01-04-01B. Grab Purge Sampling Apparatus (3 liters) (Reference 058).

01-01-04-02

Plastic bags of various compositions are suitable for the collection of flue gas grab samples. Typical apparatus includes a standard probe which is connected to an air movement device, followed by the sampling line leading to the inflatable plastic sample bag (usually Mylar, Tedlar, etc.) See Table 01-01-04-02A for some storage properties of gases in plastic bags.

A) OPERATIONAL SCOPE

B) INTERFERENCES/LIMITATIONS

C) RECOMMENDED USE AREA

5. OPERATIONAL PARAMETERS

- ## 6. REAGENTS REQUIRED

7. EQUIPMENT REQUIRED

8. KEYWORD INDEX: Flue gas sampling, grab sampling, plastic bags, Tedlar, Mylar.

9. CROSS REFERENCE ID NUMBERS 01-05-04-02; 02-02-01; 02-03-01.

10. REFERENCES

A) PRIMARY SOURCE

- ## B) BACKGROUND INFORMATION

- 024 ASTM Committee D-19 and D-23, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1605-60, "Sampling
Atmospheres for Analysis of Gases and Vapors," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 351-2.
060 Altschuler, A.P., I.R. Cohen, S.F. Selva and A.F. Wartburg, "Storage of Vapors and Gases in Plastic Bags,"
Int. J. Air Wat. Poll., 6, 75-81 (1962).
061 Conner, W.D., and J.S. Nader, "Air Sampling with Plastic Bags," Amer. Indust. Hyg. Assoc. J., 25, 291-297 (1964).
062 Baker, R.A., and R.C. Doerr, "Methods of Sampling and Storage of Air Containing Vapors and Gases," Int. J. Air
Poll., 2, 142-158 (1959).
063 Ringold, A., R. Finn, J.R. Goldsmith, H.L. Helwig and F. Schuett, "Estimating Recent Carbon Monoxide Exposures,"
Arch. Environ. Health, 5, 38-48 (1962).

TITLE FLUE GAS GRAB SAMPLING USING PLASTIC BAGS (CONTINUED)

ID NO. 01-01-04-02

B) BACKGROUND INFORMATION

- 064 Tamplin, B., Unpublished data, Air and Industrial Hygiene Laboratory, California State Department of Public Health (1963).
 065 Schuette, F.J., Unpublished data, Air and Industrial Hygiene Laboratory, California State Department of Public Health (1962).
 066 Schuette, F.J., "Plastic Bags for Collection of Gas Samples," A.I.H.L. Report No. 19, California Department of Public Health (December 1965).

C) FIELD APPLICATIONS

- 067 "Tentative Method for Analysis of C₁ through C₅ Atmospheric Hydrocarbons," Review Draft (1965) Method SDPH: 1-50, Air and Industrial Hygiene Laboratory, California State Department of Public Health.
 068 Steward, R.D., D.S. Erley, M.H. Gay, C.L. Hake, and J.E. Peterson, "Observations on the Concentrations of Trichloroethylene in Blood and Expired Air Following Exposure of Human," Amer. Indust. Hyg. Assoc. J., **23**, 167-170 (1962).
 069 O'Keefe, A.E., 1965, Private communication, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, U.S. Public Health Service, Cincinnati, Ohio.
 070 Wilson, K.W., and H. Buchberg, "Evaluation of Materials for Controlled Air Reaction Chambers," Indust. Eng. Chem., **50**, 1705-1708 (1958).

Table 01-01-04-02A. Some Storage Properties of Vapors and Gases in Plastic Bags (Reference 026).

Plastic Film	Reference	Gas or Vapor Stored	Concentration	Remarks
Mylar	060, 061	Ozone	70 ppm	10% loss in 5 hrs in synthetic air
	060, 061	NO ₂	0.2 to 0.5 ppm	5% in 8 hrs in synthetic air
	060, 061	SO ₂	0.5 ppm	Stable for 4 hrs in synthetic air
Polyvinyl	063	CO ₂	1 to 100 ppm	Storage variable with source of supply
Scotch Pak	064	CO ₂	1 to 100 ppm	Stable several days in expired air
Kel-F	062	NO ₂	1 ppm	Stable for 120 hrs

1. TITLE HIGH PRESSURE GAS GRAB SAMPLING (NATURAL GAS CONTAINING HYDROCARBONS AND NITROGEN; SULFUR; CO ₂)	2. IDENTIFICATION CODE 01-01-04-03
3. ABSTRACT OF METHODOLOGY For collecting relatively large samples in high pressure containers, the apparatus depicted in Figures 01-01-04-03A and 01-01-04-03B are used; for the collection of very large samples, several containers of sample may be simultaneously collected using a manifold system. The valves leading from the gas mains (flues) shown in the figures can be substituted with probes and lines (Teflon or 316 SS). An average sample can be obtained by taking a series of consecutive grab samples, using air or liquid displacement techniques. Alternatively, a continuous sampling method having direct connection to analytical instrumentation can be used.	
4. APPLICATION: Environmental assessment, engineering evaluation R&D A) OPERATIONAL SCOPE Method is applicable to gasifier streams, having gas under pressure as high as 9,000 - 10,000 psi. Inorganic gases, acid gases and sulfur compounds can be sampled (see Table 01-05-04-01A). B) INTERFERENCES/LIMITATIONS Proper sampling will reflect consideration of constituents present in the gas. For sampling sulfur-containing gases, air displacement methods and aluminum tanks should be used. For gases containing greater than 0.5% CO₂, an air displacement method must be used. C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment high pressure gas grab sampling procedure.	
5. OPERATIONAL PARAMETERS A) RANGE Range is governed by size and design of sample containers, and of other components of sampling equipment. Typical flue gas sampling rate of 2 to 10 m³ over a 1- to 4-hour period is applicable. B) ACCURACY N/Q C) PRECISION ±10%	
6. REAGENTS REQUIRED Mercury or other liquid for liquid displacement methods.	7. EQUIPMENT REQUIRED Sampling connections (threaded or welded pipe), sampling lines (iron pipe, copper, brass or aluminum tubing, high pressure hose; glass, quartz or porcelain tubing for low gas pressures), sample containers (iron, steel or glass - see Figure 01-01-04-01A).
8. KEYWORD INDEX: Gas grab sampling, air displacement, liquid displacement, high pressure.	
9. CROSS REFERENCE ID NUMBERS 01-05-04-01; 01-01-04-01; 02-02-01; 02-03-01.	
10. REFERENCES A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D1145-53, "Standard Method of Sampling Natural Gas," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 208-221. B) BACKGROUND INFORMATION 071 Altieri, V.J., "Gas Analysis and Testing of Gaseous Materials," American Gas Association, p. 76-79. C) FIELD APPLICATIONS	

TITLE HIGH PRESSURE GAS GRAB SAMPLING (NATURAL GAS CONTAINING HYDROCARBONS AND NITROGEN; SULFUR; CO₂) (CONTINUED)

ID NO. 01-01-04-03

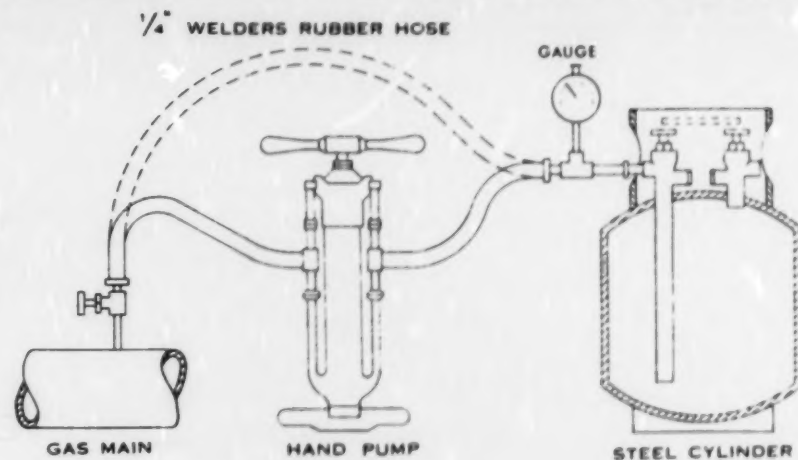
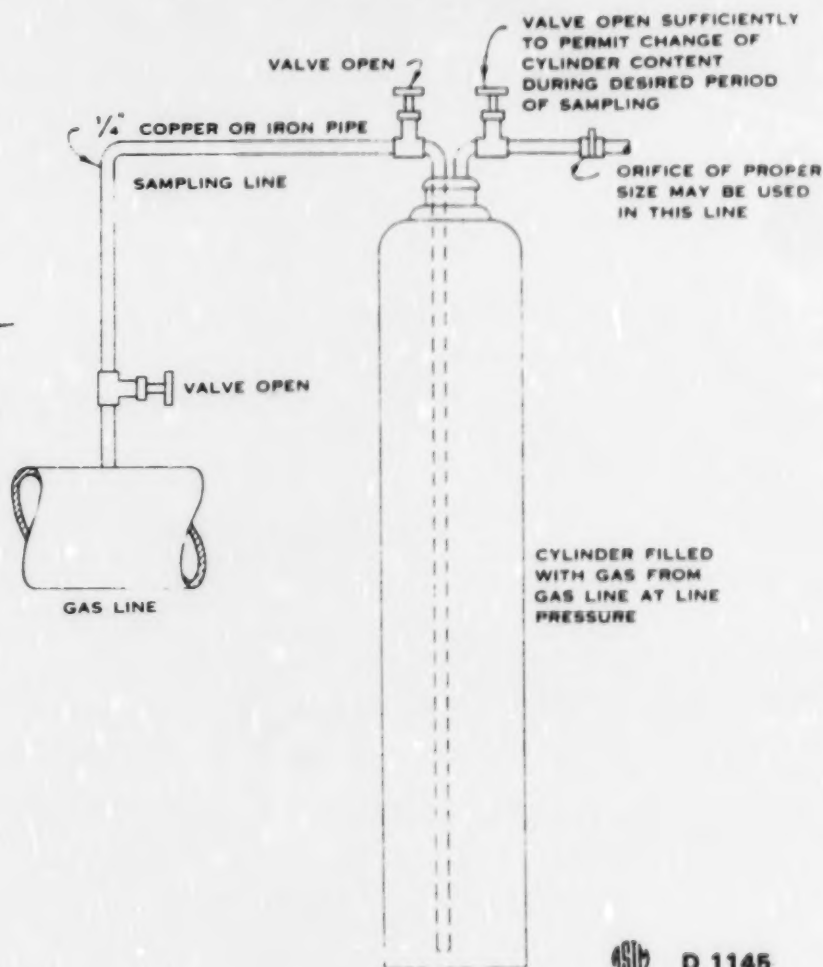


Figure 01-01-04-03A. Apparatus for Collecting a Sample in a Steel Container Under Pressure, Either Direct from Gas Main or Using a Hand Pump (057).



D 1145

Figure 01-01-04-03B. Arrangement of Apparatus for Collecting an Average Sample, Dry, Under Pressure (057).

Table of Contents for 01-02 Sampling Liquid/Slurry

01-02-01 Automatic Liquid/Slurry Sampling

01-02-01-01 Sampling Liquid Streams with a CVE Composite
Sampler

01-02-01-02 Model 1680 Sequential Liquid Slurry Sampler . .

01-02-01-03 Liquid Sampling of Lines or Tanks Using
Model L Sampler

01-02-02 Liquid/Slurry Grab Sampling

01-02-02-01 Grab Sampling of Water

01-02-02-02 Liquid/Slurry Grab Sampling (Dipper Sampling,
Thief Sampling)

APPLICATION MATRIX FOR 01-02 LIQUID/SLURRY SAMPLING

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
01-02-01-01	●		●
01-02-01-02	●		●
01-02-01-03	●		●
01-02-02-01	●		
01-02-02-02	●		

SAMPLING LIQUID AND SLURRY ID No. 01-02

Wastewater from plants consists of both contaminated and relatively clean effluent streams. In general, the contaminated wastewaters are those taken from processes while the clean wastewaters are those used for indirect heat exchange, general washing, etc. Sources of contaminated wastewaters include:

- Brines from electrolysis and crystallization
- Filter cake washings (mining operations)
- Waste acid and alkaline streams (wet scrubber equipment)
- Washing streams containing substantial amounts of suspended particulate matter (coal gasifiers).

In general, these waters are characterized by suspended solids ranging from tenths to tens of percent of the total weight.

Clean wastewaters are primarily composed of steam condensate and cooling water. Normally, these are released into the environment with little or no treatment. Due to process leaks, makeup water, boiler blow-down, etc., these streams can become polluted and would be sources for sampling.

An important factor which must be considered in sampling liquid/slurry streams is the size of sample required. There are two principal requirements which determine how much sample must be collected. The first requirement is that the amount of sample collected must be sufficient for the testing and analysis procedures to furnish an accurate and precise result. The second requirement, which determines the amount of sample to be collected, is the statistical sampling error that can be tolerated. The minimum sample required for analysis varies considerably for the trace analysis. The minimum element concentration level varies between 1 and 1000 μg for most analysis procedures. For the lower ppm concentration levels of interest, this translates into minimum sample volumes ranging between one ml and one liter. This range of sample volumes is easily within the operating limits of presently available liquid sampling equipment and presents no special difficulties.

Determining the minimum size liquid sample that must be collected to reduce statistical sampling error to acceptable limits is considerably more difficult. The total error of sampling and analysis is equal to:

$$E_T = \sqrt{(S)^2 + (A)^2}$$

Where E_T = the total error of the combined sampling and analysis

S = error in sampling

A = error in analysis

For example, to meet a goal of a combined relative sampling and analysis error of ± 25 percent, the allowable error between sampling and analysis must be budgeted. Allowing a maximum 15 percent error for analysis, the sampling error can be as high as 20 percent and meet the 25 percent overall error ($25 = \sqrt{20^2 + 15^2}$).

The equipment discussed in this section is capable of handling the wide variety of process streams found in most industrial applications. In streams with highly corrosive materials present, the Teflon coating all metal parts to prevent contamination of the samples and destruction of the sampling system should be considered. However, for most applications, the built-in flexibility of the off-the-shelf samplers is adequate.

01-02-01 Automatic Liquid/Slurry Sampling
(Abstracts 01-02-01-01 through 01-02-01-03)

The factors which must be considered in accurately sampling a liquid/slurry stream include:

- Stream homogeneity
- Stream flow rate and variations
- Prevention of sample loss
- Sources of contamination
- Sample size required.

Of these, stream homogeneity is perhaps the most important factor. Unlike stack effluent streams which are mixed fairly evenly due to higher thermal agitation and lower fluid viscosities, liquid streams tend to be

more stratified and require more careful sampling. A flow-proportional composite sampling technique is required for sampling liquid and slurry streams for trace materials. In obtaining a composite representative sample from a stack, a traverse of the pipe or duct is made. This is usually impractical in sampling liquid streams. In liquid streams, a composite sample (01-02-01-01, 02) can be taken by using several differently positioned probes, a single multi-ported probe, or a combination of these. While any of these approaches is suitable, the single multi-ported sampler is usually more convenient.

In the case of slurry sampling, it is also important to avoid segregation of liquid and solid phases. This is similar to the requirement for isokinetic sampling in particulate-laden gas streams. Sampling velocity is the most critical factor in sampling sewage slurries. The EPA (Reference 072) has shown that suction line velocity is only one of many variables, and that line velocity differences within a reasonable range (approximately 0.6-1.5 m/sec or 2 to 5 ft/sec) do not have a consistent effect on sample composition. Outside of this range, certain low velocity piston or peristaltic pumps and high velocity vacuum samplers often preclude large composition deviations. In other cases such as storage tanks or pipes under high pressure, pumps are not necessary. Special samplers (01-02-02-03) are available for this specialized purpose.

01-02-02 Liquid/Slurry Grab Sampling
(Abstracts 01-02-02-01 through 01-02-02-02)

Grab sampling of tap water (01-02-02-01) requires that the tap and any associated lines are purged completely. A sample can then be taken or composited over a period of time. Free flowing streams (01-02-02-02) simply require that the sample container be positioned so that a portion is collected from the full cross-section of the stream. Because composition can vary with depth in storage tanks or tank cars, samples should be taken at depths representing the midpoint of the upper, middle, and lower parts of the tank (01-02-02-02).

Trace materials in liquid phases may be lost from a sample through adsorption on sampling line or reservoir surfaces. Borosilicate glass

(Pyrex) surfaces appear to be particularly effective in removing trace heavy metals, especially under alkaline conditions. Plastics such as polyethylene, polypropylene, and Teflon show little or no tendency to adsorb inorganic materials. It is essential, therefore, that the sampling lines and collection reservoirs (01-02-02-01) used for sampling liquid streams be made of plastic, preferably Teflon because of its superior chemical inertness toward strong acids and alkalis and other chemical reagents.

Just as material may be lost from a sample due to surface effects, so may a sample be contaminated with elements from those surfaces. Surface wall material can be deposited in a sample either by a chemical extraction of the wall materials by reagents in the sample or by physical abrasion or erosion of the wall by a sample. The latter case can be a significant problem for slurry systems because of the chemical interaction of the sample with wall materials and the possibility that a sample could become contaminated with elements from a sample probe or a sample line. The proper cleaning procedures must be followed (see 02-01).

REFERENCES

- 072 Shelley, P.E., and G. A. Kirkpatrick, "An Assessment of Automatic Flow Samples," EPA Report R2-73-261 (1973).

1. TITLE SAMPLING LIQUID STREAMS WITH A CVE COMPOSITE SAMPLER		2. IDENTIFICATION CODE 01-02-01-01
3. ABSTRACT OF METHODOLOGY		
The vacuum system lifts liquid through a suction line into the sampling chamber. When filled, the chamber is automatically closed to the vacuum. The pump then shuts off and the sample is forcibly drawn into the sample container. A secondary float check prevents any liquid from reaching the pump, should the primary shutoff pass any material. The suction line drains by gravity back into the source. No pockets of fluid remain to contaminate subsequent samples. Automatic blowdown of suction lines and the entire liquid system assures that no material remains to contaminate the current sample (see Figure 01-02-01-01A).		
4. APPLICATION: Engineering evaluation R&D, environmental assessment		
A) OPERATIONAL SCOPE This sampler can be used in flowing streams with dissolved salts, in open channels, partially full pipe flows with sampling port greater than 0.64 cm (1/4 inch) ID, full pipe flows at atmospheric pressure, flowing streams (open channel and flows with suspended solids of 0.32 cm (1/8 inch) particle size or less). This instrument also can sample to a maximum depth of 6.96 m (20 feet). B) INTERFERENCES/LIMITATIONS This instrument is designed to operate at temperatures less than 200°C. Between 20 to 50 ml-sized samples per cycle can be taken, up to a total of the gallon storage capacity. C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D liquid/slurry sampler.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY This instrument was evaluated by the EPA as the best liquid/slurry automatic sampler (see Table 01-02-01-01A). C) PRECISION N/A		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
None		Model CVE liquid slurry sampler (Quality Control Equipment Corp., Des Moines, Iowa).
8. KEYWORD INDEX: Sampling, liquid slurry sampling, CVE sampler.		
9. CROSS REFERENCE ID NUMBERS 02-01-02, 02-01-03.		
10. REFERENCES		
A) PRIMARY SOURCE 072 Shelley, P.E., and G.A. Kirkpatrick, "An Assessment of Automatic Flow Samplers," EPA R2-73-261 (1973). B) BACKGROUND INFORMATION C) FIELD APPLICATIONS 073 Harris, J., and W.J. Kaefer, "Wastewater Sampling Methodologies and Flow Measurement Techniques," EPA-907/9-74-005, June 1974.		

TITLE SAMPLING LIQUID STREAMS WITH A CVE COMPOSITE SAMPLER (CONTINUED)

ID NO. 01-02-01-01

Table 01-02-01-01A. Incidence of Sampler Malfunction*

Automatic Wastewater Sampler	Total Times Used	Total Times Failed	Overall Failure Rate Percent	Influent Sampling Stations			Effluent Sampling Stations		
				Used	Failure	Failure Rate Percent	Used	Failure	Failure Rate Percent
Sigmamotor WA-2	24	6	25	8	4	50	16	2	13
Sigmamotor WD-2	31	4	13	15	2	13	16	2	13
Brailsford DU-1	45	15	33	40	13	33	5	2	40
Brailsford EV-1	29	5	17	26	5	19	3	0	0
Brailsford EP-1	63	6	10	55	6	11	8	0	0
QCEC CVE	90	4	4	77	4	5	13	0	0
Pro-Tech C6-125P	10	4	40	NOT BROKEN DOWN					
ISCO 1391-X	16	4	25	16	4	25	0	0	0
ISCO 1392	17	1	5	15	1	7	2	0	0
N-Con Scout	14	2	14	14	2	14	0	0	0
N-Con Surveyor	7	3	43	5	3	60	2	0	0
Total and Mean Failure Rates	346	54	16	271	44	16	65	6	9

*From Harris and Keefer (see Field Applications Reference 073)

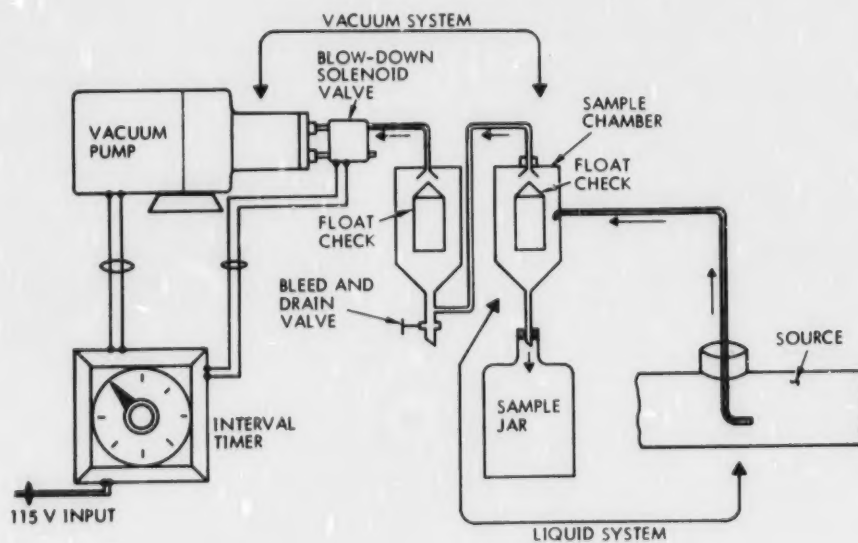


Figure 01-02-01-01A. Schematic of CVE Composite Sampler.

1. TITLE MODEL 1680 SEQUENTIAL LIQUID/SLURRY SAMPLER	2. IDENTIFICATION CODE 01-02-01-02
3. ABSTRACT OF METHODOLOGY	
Samples can be collected at intervals of 1 to 999 minutes with a maximum sample size of 500 ml. While 28 bottles (see 02-01-01-05) are provided, 1 to 4 samples may be added to each bottle to provide a limited compositing capability with the sequential sampling. An ice compartment has adequate capacity to keep the samples 4.4°C below ambient temperature for 12 hours (-1.1°C for 24 hours). The samples are collected using a peristaltic pump with valves on metering chambers, which minimizes equipment failure and sample contact.	
4. APPLICATION: Engineering evaluation R&D, environmental assessment	
A) OPERATIONAL SCOPE This instrument can be used in flowing streams, dissolved salts and open channel flows, partially-filled pipe fills with sampling ports greater than 1.27-cm (1/2 inch) ID, full pipe flows at atmospheric pressure, flowing streams (open channels and closed) with suspended solids (0.32-cm or 1/8-inch particle size). The maximum depth of sampling is 6.96 m (20 ft). B) INTERFERENCES/LIMITATIONS This unit is designed to sample streams at temperatures less than 200°C. Each sample bottle contains up to 500 ml with a total of 28 bottles. Because of the arrangement of the bottles, the ice cooling capability is less effective. C) RECOMMENDED USE AREA This unit is second choice as an engineering evaluation R&D liquid/slurry sampler.	
5. OPERATIONAL PARAMETERS	
A) RANGE N/A B) ACCURACY The Model 1680 was also highly recommended in an EPA assessment study. It is currently being used in the Los Angeles County district. C) PRECISION N/A	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
None	Model 1680 sequential liquid/slurry sampler (Instrumentation Specialties, Co., Lincoln, Nebr.).
8. KEYWORD INDEX: Sampling, liquid sampling, sequential sampling.	
9. CROSS REFERENCE ID NUMBERS 02-01-01-05, 02-01-02, 02-01-03.	
10. REFERENCES	
A) PRIMARY SOURCE 072 Shelley, P.E., and G.A. Kirkpatrick, "An Assessment of Automatic Flow Sampler," EPA Report Number R2-73-261 (1973). B) BACKGROUND INFORMATION C) FIELD APPLICATIONS 073 Harris, D.J., and W.J. Keefer, "Wastewater Sampling Methodologies and Flow Measurement Techniques," EPA 907/9-74-005, June 1974.	

1. TITLE LIQUID SAMPLING OF LINES OR TANKS USING MODEL L SAMPLER	2. IDENTIFICATION CODE 01-02-01-03
3. ABSTRACT OF METHODOLOGY The Model L sampling probe (see Figure 01-02-01-03A) is moved by an air cylinder in and out of the liquid line or tank. Machined to a fine tolerance, this air liquid sampler has long-life Teflon seals that will keep it leakproof. Samples are gravity expelled into receptacles under the unit. No residual is left behind to foul succeeding samples. Quantity of the sample ranges from 2 ml to 30 ml. It is constructed of 316 SS and can be mounted through a side wall or a pipe or tank or at an elbow. This type of sampler is extremely useful if sampling lines have access ports already available.	
4. APPLICATION: Environmental assessment, engineering evaluation R&D. A) OPERATIONAL SCOPE This sampler is designed to sample liquids in a pipe or in a tank containing liquids that are compatible with 316 SS. This system is particularly useful if the liquid is under pressure at the sampling point. B) INTERFERENCES/LIMITATIONS Since the sampler is constructed of 316 SS, contamination through corrosion of the SS by corrosive liquids is possible. Contamination of the collected sample by the corrosion products of 316 SS (Ni, Cr and Fe) should be considered prior to using this sampler. C) RECOMMENDED USE AREA Environmental assessment of pressurized lines.	
5. OPERATIONAL PARAMETERS A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED Sampling bottles (see 02-01-01).	7. EQUIPMENT REQUIRED Type L liquid sampler (Quality Control Liquid Company, Des Moines, Iowa).
8. KEYWORD INDEX: Liquid sampling, Type L sampler.	
9. CROSS REFERENCE ID NUMBERS 02-01-01, 02-01-02.	
10. REFERENCES A) PRIMARY SOURCE 074 Manufacturer's Bulletin on Type L Sampler from Quality Control Equipment Co., 2505 McKinley Avenue, Des Moines, Iowa 50315. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D510-68, "Standard Methods of Sampling Distilled Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 2. 025 Brown, E., M.J. Fishman and N.W. Skougstad, "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," U.S. Geological Survey, Technical Water Resources Inventory, 5, Chapter A1, 1970. C) FIELD APPLICATIONS 072 Shelley, E.E., and G.A. Kirkpatrick, "An Assessment of Automatic Flow Samplers," EPA Report Number R2-73-261 (1973).	

TITLE LIQUID SAMPLING OF LINES OR TANKS USING MODEL L SAMPLER (CONTINUED)

ID NO. 01-02-01-03

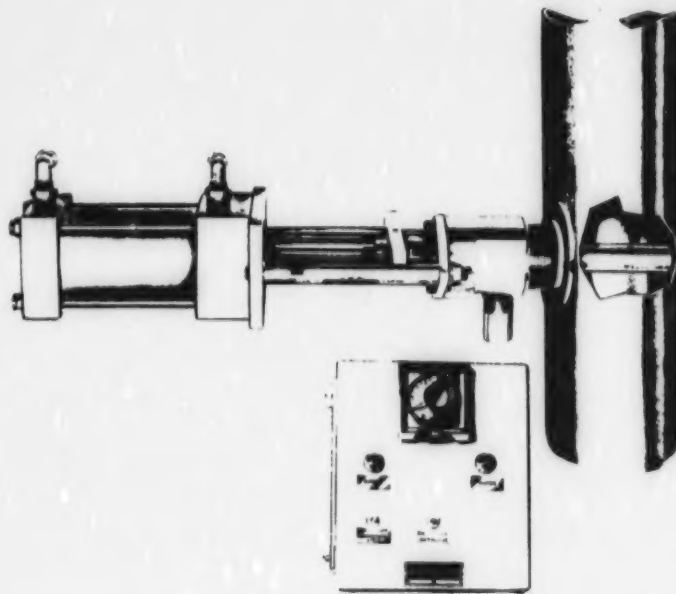


Figure 01-02-01-03A. Model L Sampling Probe (Quality Equipment Co.).

2. IDENTIFICATION CODE

01-02-02-01

1. TITLE GRAB SAMPLING OF WATER

3. ABSTRACT OF METHODOLOGY

A tap sampling assembly is shown in Figure 01-02-02-01A. Before sampling, the tap and associated lines must be thoroughly flushed to avoid contamination. A clean delivery tube is then connected to the tap, and a sample of 0.25 liters or more per hour can be collected. When sampling from cocks or valves, the flow is conducted through a sampling line or a polyethylene tube extension of the sampling line to the sample bottle until it reaches the bottom. A volume of 10 times the volume of the sample container is then allowed to flow before a sample is taken.

Depth samples are obtained using the standard depth sampling rigs (e.g., Sirco Uniscoop). The sampler is typically lowered into the sample using nylon rope or plastic-coated wire to a desired depth, after which a messenger weight can be lowered to trip a valve-closing mechanism.

Samples at low or subatmospheric pressures can be obtained by inserting a water-cooled condenser, and a pump or aspirator between the flue and the sample container. The volumes of sample required for some typical analyses are shown in Table 01-02-02-01A.

4. APPLICATION: Environmental assessment.

A) OPERATIONAL SCOPE

Method is applicable to sampling most industrial aqueous streams. The tap sampling procedure is applicable to sampling liquids of 11.8 kg (1.83 kgf/cm²) Reid vapor pressure or less.

B) INTERFERENCES/LIMITATIONS

Special precautions may be required for handling of water containing unstable constituents, including those marked with an asterisk in Table 01-02-02-01A.

C) RECOMMENDED USE AREA

This is the recommended level 1 environmental assessment procedure for aqueous grab sampling.

5. OPERATIONAL PARAMETERS

- A) **RANGE** Range depends on size and/or type of apparatus used; see Table 01-02-02-01A for partial listing of volume requirements. Sampling rates will conform to flow rate of the sampled stream. Depth samples may be obtained from any desired depth.
- B) **ACCURACY** N/Q
- C) **PRECISION** $\pm 10\%$, if proper sampling procedures for obtaining representative samples are followed.

6. REAGENTS REQUIRED

Cleaning solutions (solvents, soap, etc.); reagent water for rinsing sample containers.

7. EQUIPMENT REQUIRED

Sampling apparatus as shown in Figures 01-02-02-01A, B; delivery tubes; sample containers.

8. **KEYWORD INDEX:** Grab sampling, water, tap sampling, depth sampling (Kemmerer type), reduced pressure samples.

9. **CROSS REFERENCE ID NUMBERS** 02-02; 02-03.

10. REFERENCES

A) PRIMARY SOURCE

- 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D510-68, "Standard Methods of Sampling Industrial Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 2-17.
- 015 ASTM Committee D-2 and F-17, "Petroleum Products - LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," 1971 Annual Book of ASTM Standards, Part 18, D270-65, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 47-71.
- 058 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Process Measurements, Lurgi Coal Gasification Process," TRW Systems Group, EPA Contract No. 68-02-1412, March 1975, p. 8-7.

B) BACKGROUND INFORMATION

- 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1192-70, "Standard Specification for Equipment for Sampling Water and Steam," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 190-195.
- 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1193-70, "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 196-7.

C) FIELD APPLICATIONS

TITLE GRAB SAMPLING OF WATER (CONTINUED)

ID NO. 01-02-02-01

Table 01-02-02-01A. Volume of Sample Required for Determination of the Various Constituents of Industrial Water (Reference 024).

Specific Determination	Volume of Sample, ^a ml	Specific Determination	Volume of Sample, ^a ml
Physical Tests		Cations:	
*Color and odor	100 to 500	Aluminum, Al ⁺⁺⁺	100 to 1000
*Corrosivity	flowing sample	+Ammonium, NH ₄ ⁺	500
*Electrical conductivity	100	Antimony, Sb ⁺⁺⁺ to Sb ⁺⁺⁺⁺	100 to 1000
*pH, electrometric	100	Arsenic, As ⁺⁺⁺ to As ⁺⁺⁺⁺	100 to 1000
Radioactivity	100 to 1000	Barium, Ba ⁺⁺	100 to 1000
*Specific gravity	100	Cadmium, Cd ⁺⁺	100 to 1000
*Temperature	flowing sample	Calcium, Ca ⁺⁺	100 to 1000
*Toxicity	100 to 20 000	Chromium, Cr ⁺⁺⁺ to Cr ⁺⁺⁺⁺⁺	100 to 1000
*Turbidity	100 to 1000	Copper, Cu ⁺⁺	200 to 4000
Chemical Tests		+Iron, Fe ⁺⁺ and Fe ⁺⁺⁺	100 to 1000
Dissolved Gases:		Lead, Pb ⁺⁺	100 to 4000
+Ammonia, NH ₃	500	Magnesium, Mg ⁺⁺	100 to 1000
+Carbon dioxide, free CO ₂	200	Manganese, Mn ⁺⁺ to Mn ⁺⁺⁺⁺⁺	100 to 1000
+Chlorine, free Cl ₂	200	Mercury, Hg ⁺ and Hg ⁺⁺	100 to 1000
+Hydrogen, H ₂	1000	Potassium, K ⁺	100 to 1000
+Hydrogen sulfide, H ₂ S	500	Nickel, Ni ⁺⁺	100 to 1000
+Oxygen, O ₂	500 to 1000	Silver, Ag ⁺	100 to 1000
+Sulfur dioxide, free SO ₂	100	Sodium, Na ⁺	100 to 1000
Miscellaneous:		Strontium, Sr ⁺⁺	100 to 1000
Acidity and alkalinity	100	Tin, Sn ⁺⁺ and Sn ⁺⁺⁺⁺	100 to 1000
Bacteria, iron	500	Zinc, Zn ⁺⁺	100 to 1000
Bacteria, sulfate-reducing	100	Anions:	
Biochemical oxygen demand	100 to 500	Bicarbonate, HCO ₃ ⁻	100 to 200
Carbon dioxide, total CO ₂ (including CO ₃ ⁻ , HCO ₃ ⁻ and free)	200	Bromide, Br ⁻	100
Chemical oxygen demand (dichromate)	50 to 100	Carbonate, CO ₃ ⁻⁻	100 to 200
Chlorine requirement	2000 to 4000	Chloride, Cl ⁻	25 to 100
Chlorine, total residual Cl ₂ including OC, HOCl, NH ₂ Cl, NHC ₂ Cl ₂ , I ₂ and free	200	Cyanide, CN ⁻	25 to 100
Hardness	50 to 100	Fluoride, F ⁻	200
Microorganisms	100 to 200	Hydroxide, OH ⁻	50 to 100
Volatile and filming amines	500 to 1000	Iodide, I ⁻	100
pH, colorimetric	10 to 20	Nitrate, NO ₃ ⁻	10 to 100
Polyphosphates	100 to 200	Nitrite, NO ₂ ⁻	50 to 100
Silica	50 to 1000	Phosphate, ortho, PO ₄ ⁻⁻⁻ , HPO ₄ ⁻⁻ , H ₂ PO ₄ ⁻	50 to 100
Solids, dissolved	100 to 20 000	Sulfate, SO ₄ ⁻⁻ , HSO ₄ ⁻	100 to 1000
Solids, suspended	50 to 1000	Sulfide, S ⁻⁻ , HS ⁻	100 to 500
		Sulfite, SO ₃ ⁻⁻ , HSO ₃ ⁻	50 to 100

^aVolumes specified in this table should be considered as a guide for approximate quantity of sample necessary for the particular analysis. The exact quantity used should be consistent with the volume prescribed in the standard method of analysis, whenever the volume is specified.

^bAliquot may be used for other determination.

^cSamples for unstable constituents must be obtained in separate containers, preserved as prescribed, completely filled and sealed against all exposure.

TITLE GRAB SAMPLING OF WATER (CONTINUED)

ID NO. 01-02-02-01

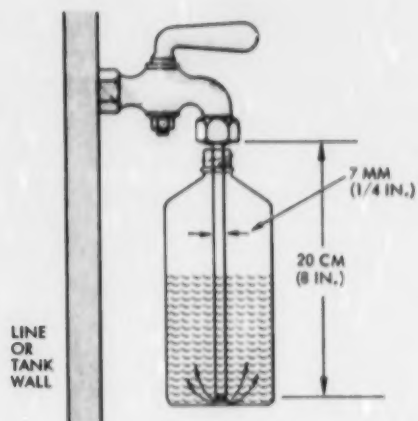
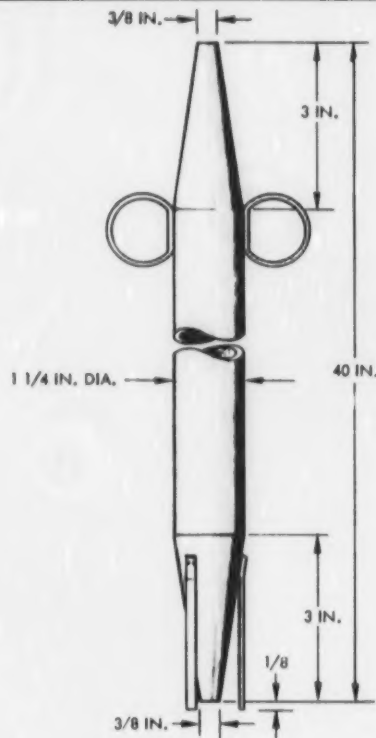


Figure 01-02-02-01A. Assembly for Tap Sampling (Reference 05B).

1. TITLE LIQUID/SLURRY GRAB SAMPLING (DIPPER SAMPLING, THIEF SAMPLING)		2. IDENTIFICATION CODE 01-02-02-02
3. ABSTRACT OF METHODOLOGY		
Dipper sampling can be conducted by using a dipper having a flared bowl and adequate capacity for the sample to be collected. The dipper is inserted into a free-flowing stream so that a portion is collected from a full cross-section of the stream. Sampling is conducted at time intervals such that a representative sample is collected (see 01-02). Thief samplers (shown in Figures 01-02-02-02A, B) should be lowered into the dome of a tank car or hatch at depths representing the midpoint of the upper, middle and lower parts of the tank. When full, the thief is removed and the contents are transferred to a sample container. Continuous sampling methods (discussed in 01-02-01) can also be used to obtain grab samples, except that only a single 1-liter sample is needed.		
4. APPLICATION: Environmental assessment		
A) OPERATIONAL SCOPE Method is applicable to sampling most noncorrosive liquids. The dipper method is applicable for sampling liquids of 0.91 kg (0.4 kgf/cm ²) Reid vapor pressure or less, and for semi-liquids where an open discharge stream exists; the thief procedure is applicable to obtaining bottom samples or semi-liquids in storage tanks.		
B) INTERFERENCES/LIMITATIONS Some limitations on obtaining representative samples include cleanliness of the sample container and use of proper sampling procedure.		
C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment method for liquid/slurry grab sampling of process effluent.		
5. OPERATIONAL PARAMETERS		
A) RANGE Range is dependent upon size and type of sampling equipment used. Sampling rate, governed by stream rate, is virtually limitless. Apparatus should be designed such that proper depth is sampled.		
B) ACCURACY N/Q		
C) PRECISION ±10-20%		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Cleaning solutions (solvents, such as naphtha soap solutions).		Sampling apparatus as shown in Figures 01-02-02-02A and B; delivery tubes; sample containers.
8. KEYWORD INDEX: Grab sampling, liquid sampling, slurry sampler, dipper sampler, thief sampler.		
9. CROSS REFERENCE ID NUMBERS 01-02; 02-02; 02-03.		
10. REFERENCES		
A) PRIMARY SOURCE 015 ASTM Committee D-2 and F-7, "Petroleum Products - LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," 1971 Annual Book of ASTM Standards, Part 18, D270-65, American Society for Testing and Materials, Philadelphia, PA., 1971, P. 47-71.		
B) BACKGROUND INFORMATION 015 ASTM Committee D-2 and F-7, "Petroleum Products-LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," 1971 Annual Book of ASTM Standards, Part 18, D1265, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 256-258. 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements, Trace Inorganic Materials," TRW Systems Group, EPA No. 68-02-1412, July 1975, p. 8-9.		
C) FIELD APPLICATIONS		

TITLE LIQUID/SLURRY GRAB SAMPLING (DIPPER SAMPLING, THIEF SAMPLING)
(CONTINUED)

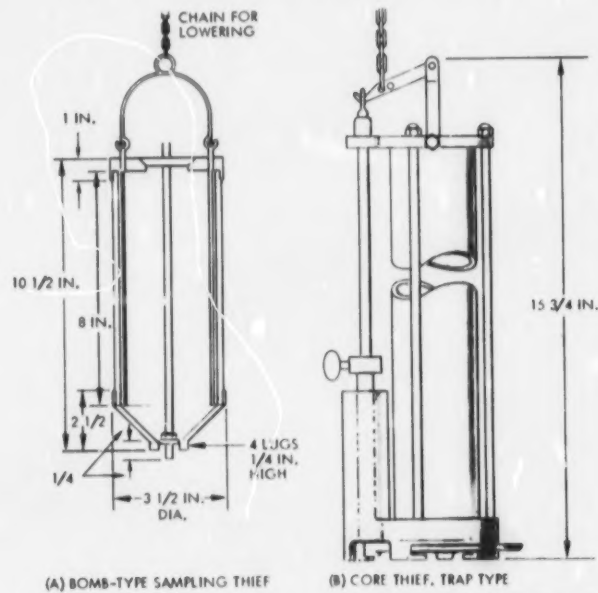
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METRIC EQUIVALENTS

IN.	1/8	3/8	1 1/4	40
MM	3	10	32	1016

Figure 01-02-02-02A. Sampling Thief or Tube (Reference 01P).



(A) BOMB-TYPE SAMPLING THIEF

(B) CORE THIEF, TRAP TYPE

METRIC EQUIVALENTS

IN.	1/4	1	2 1/2	3 1/2	8	10 1/2	15 3/4
MM	7	25	64	89	203	267	400

Figure 01-02-02-02B. Sampling Thief. (Reference 01B).

Table of Contents for 01-03 Sampling Solids

01-03-01 Automatic Solid Sampling

01-03-01-01 Sampling Solid Materials With a Pneumatic
Sampler

01-03-01-02 Sampling of Solids (Coal) Using Standard
Mechanical Methods

01-03-02 Solid Grab Sampling

01-03-02-01 Solids Grab Sampling (Long-Pile, Alternate
Shovel Method)

APPLICATION MATRIX FOR 01-03 SOLID SAMPLING

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
01-03-01-01	●		●
01-03-01-02	●		
01-03-02-01	●		●

SAMPLING SOLIDS ID No. 01-03

Solid sampling covers a broad spectrum of material sizes from large lumps down to powders and dusts. There is an equally diverse assortment of potential sample sites including railroad cars, large heaps, plant hoppers, conveyor belts, and process stream pipes. Obviously no one method or piece of equipment can cover all of the situations that could be encountered. One needs to be aware of the advantages and disadvantages of all the procedures and then select whichever is most appropriate for each field test. The discussion presented in this section is a brief overview of common solid sampling situations and of some of the alternatives available to a field test team.

The chief consideration of solid sampling methodology is the problem of acquiring representative samples. There are several procedures for shovel sampling which attempt to make the sampling as representative as possible. A statistical means of determining the sample size needed to yield results having a prescribed level of precision based on the above factors has been derived theoretically (Reference 076).

The general form of this equation is:

$$n = \left(\frac{t\sigma}{E} \right)^2$$

where:

n = number of units to be taken for sample

σ = advance estimate of the standard deviation

E = maximum allowable difference between the result to be obtained from the sample and the result of testing the entire bulk of material

t = a factor corresponding to the acceptable risk of exceeding E

The terms " E " and " t " are relatively easy to assign as they are the parameters of the desired precision. The t is a statistical factor

expressing the probability that, by chance, E will be exceeded. The following lists values of t for a few approximate probability values:

<u>t</u>	<u>Probability that E will be exceeded</u>
3	3 in 1000
2.58	1 in 100
2	45 in 1000
1.96	1 in 20
1.64	1 in 10

Generally, a factor of 3 is used to minimize the possibility of the sampling error exceeding E. Any degree of precision can be chosen for E, bearing in mind that the sample size increases as the square of the entire precision term. E can be expressed as percent or in units of measurement; however, σ must be expressed in the same way so that the resultant, n, is unitless.

The answer then comes out as n units of sample. These units (e.g., shovelfuls, pounds, or whatever) must be the same as those used to determine the standard deviation, σ , in order to relate the two sides of the equation. This means one of two things must be done. Either a preliminary test must be run on at least 10 units of sample to calculate the standard deviation between units, or σ can be estimated, a somewhat larger number of units taken for the sample than the estimated necessary, and the sample size readjusted after the actual σ has been determined.

The following is an example of this statistical equation. Using some type of pipe sampler, a flowing stream of pulverized coal is being sampled for percent ash. A preliminary test showed the average deviation between samples taken by the pipe sampler to be 25 percent and a maximum sampling error of 10 percent is required: Then:

$$n = \left[\frac{(3)(25)}{10} \right]^2 = (7.5)^2 = 56.25$$

= 57 samples

must be taken to determine percent ash in the coal with a maximum error of 10 percent.

01-03-01 Automatic Solid Sampling
(Abstracts 01-03-01-01 through 01-03-01-02)

Sampling solids as they move through pipes is the method of choice if it is possible. There are a variety of pipe samplers commercially available. The best type of sampler of this variety is the pneumatic sampler (01-03-01-01). This sampler eliminates the screw type or scraping action of other types of samplers which grind the sample and abrade the sampler, thereby introducing considerable contamination.

Mechanical samplers (01-03-01-02) require that the sample material be in motion to present it to the cutters as a thin ribbon or stream. Design considerations for feeding these samplers and catching the sample and rejected material generally necessitate the installation of the sampler in a permanent manner into the flow stream of the sample material. Numerous mechanical samplers have been designed and the most popular designs have been variously modified to satisfy specific applications. Nevertheless, all mechanical samplers fall into two general types: those that take part of the stream all of the time (stationary samplers), and those that take all of the stream part of the time (moving samplers).

In stationary mechanical samplers, the entire sample stream is fed continuously through the device and the stationary cutting edges remove or divide out specific fractions. The two best known designs of this type are rifflers and whistle-pipes.

Riffilers take several slices of the stream by means of parallel chutes alternately placed at 90° angles to each other, thereby cutting the stream in half. Successive riffilers can be arranged in banks to cut the stream into any desired fraction. The smaller the chute width, the greater the number of increments in the sample. Therefore, the accuracy of riffiler sampling increases as the ratio of chute width to particle size decreases, to the limiting condition where the chutes tend to clog. In general, chutes should be at least three times the diameter of the largest size particle to avoid clogging. Care must be taken to feed the riffiler with a well-mixed, uniform sheet of material as any compositional variations due to cross-sectional segregation are multiplied by a bank of riffilers.

A whistle-pipe sampler consists of a vertical pipe with notched openings cut halfway through the pipe, each spaced 90° horizontally from the one above. Rectangular steel plates are placed in the notches at a 45° angle to the vertical so that the top edges coincide with a diameter of the pipe. Thus each notch halves the sample and, with a series of five openings, the sample obtained as $1/32$ of the original volume. The same fraction with improved accuracy can be obtained by using a cutter arrangement that quarters the stream, rejecting opposite quarters, and spacing each cutter at 45° horizontally from the one above. In either design, a hopper-shaped liner is placed above each notch to re-center the stream before it reaches the next cutter.

Both these stationary samplers have irresolvable design problems that reduce their reliability. Worn or bent cutting edges distort both the volume and the particle size distribution of the sample. The housing necessary for these samplers prevents examining them for clogged openings while in operation. Material streams whose composition varies along the transverse section will be further segregated by either of these samplers.

Moving samplers consist of cutters that move through the free-falling sample stream taking all the stream for the duration of time they are moving through it. There are two ways of effecting this. One is with rotating or oscillating samplers whose cutters are set on radii of an arc, and the other is with straight-line samplers whose cutting edges are set parallel to each other and perpendicular to the line of their path.

Among the well-known designs of rotating arc-path samplers are Vezins, Synders, and Chas. Synders. They all consist generally of scoops with vertical sides, set on an axis parallel to the stream flow. The best oscillating samplers are known as Bruntons. The scoop travels back and forth across the stream in a pendulum-type motion. The travel path must be sufficiently long to minimize the bias created by taking more sample from the sides of the stream than from the middle. All the arc-path samplers have the advantage over stationary samplers in that they take an accurate cut, are simply constructed, and are accessible for observation while in operation. Damp sample material may tend to clog the scoops and care must be taken to maintain the cutting edges in good condition and to keep them completely radial.

The straight-line samplers are generally considered to be the most reliable and accurate of all available types of samplers. The design of their cutters is such that the sampling scoop spends an equal amount of time in every portion of the stream. Generally the travel is at right angles to the stream. Though they provide increased reliability, these samplers require more maintenance and attention because of their increased mechanical complexity.

Thus automatic sampling will normally consist of using in-house equipment. If these types of equipment are not available, standard solid grab sampling techniques must be used.

01-03-02 Solid Grab Sampling
(Abstracts 01-03-02-01)

Grab sampling in its simplest form consists of taking small, equal portions at random or regular intervals from the mass, typically from railroad cars, large heaps, or hoppers. The method is quick and inexpensive. However, it makes no allowance for segregation due to particle size and tends to give consistently high or consistently low results depending on the person sampling. As such, grab sampling should only be used for no more than rough checking.

Coning and quartering (01-03-02-01) consists of carefully piling the material into a conical heap, then flattening the cone into a circular cake. The cake is then marked into quadrants with opposite quadrants being taken for sample and the other two discarded. The entire process can be repeated until the desired sample size is obtained. This method is time-consuming and the symmetry of the intended vertical size segregation is difficult to achieve in practice.

In fractional shoveling, (01-03-02-01) every third, fourth, fifth, or tenth shovelful is taken for sample and is applicable to materials being loaded, unloaded, or moved from one place to another by shoveling. This method is inexpensive and relatively fast. If performed conscientiously, fractional shoveling can be more reliable than coning and quartering. However, its applicability is limited and errors are easily introduced by carelessness.

Pipe borers represent another class of solid sampling methodology. The usual method for pipe borers is to insert the pipe into the material to be sampled at regular intervals. Provided that the pipe is long enough to reach the bottom of the material, the method is fairly reliable. However, it is only applicable to fine or powdered dry materials, because lumps or any stickiness will jam or plug the pipe. Small pipe borers can be used to sample sacks or cans of material. There are primarily two designs that give best results. One is a simple pipe that is tapered so the end first inserted is smaller in diameter than the handle end. A more sophisticated design, known as a thief, makes the sample more representative vertically. It consists of two close-fitting concentric pipes sealed at the base in a conical point. Longitudinal slots are cut along the side of each pipe. The thief is inserted with the slots turned away from each other and then, when the sampler is in position, the outer pipe is rotated, lining up the slots and allowing the inner pipe to fill the sample. For proper results with any design of pipe borer, whatever opening the sample material passes through (slots or circular pipe ends) must be large relative to the maximum particle size.

Auger samplers, a form of drill, pack the sample in the helical groove of the auger and can be enclosed in a casing if the nature of the sample is such that it will spill when the auger is removed from the hole. They are simple to use, like the pipe borers, and have the further advantage of being applicable to a greater variety of materials. For materials that are packed too hard for a pipe sampler to be forced in, augers work well. For very packed materials, machine-driven augers are available. However, if spill is a serious problem a thief type pipe sampler would be the better choice. Both pipe samplers and augers will yield poor results if the material being sampled is poorly mixed.

REFERENCES

- 076 Welcher, et al, "Standard Methods of Chemical Analysis," Vol. II A, 6th ed. (1963).

2. IDENTIFICATION CODE

01-03-01-01

1. TITLE SAMPLING SOLID MATERIALS WITH A PNEUMATIC SAMPLER**3. ABSTRACT OF METHODOLOGY**

The most suitable type of sampler for trace element sampling is a pneumatic sampler. This type of sampler eliminates the screwed or scrapping action of the other types of samplers which can grind the sample and abrade the sampler at the same time. This scrapping or grinding action introduces considerable contamination to the solid sampler. The best sampler currently available is the Model RTA of the Quality Control Equipment Corp. All parts in contact with the sample can be made of Teflon or nylon. The sampling tube is extended into the air line where it dwells for a short adjustment period (see Figure 01-03-01-01A). The sample is trapped in a suitably sized cavity in the sampling tube which is then automatically retracted and the sample rejected by an air blast. The sample is completely discharged and no carry-over occurs. Samples collected by this device should be stored in a prewashed and predried plastic bottle or plastic-lined drums. If plant personnel are to take the sample, they should be provided with appropriate bottles or containers.

4. APPLICATION: Engineering evaluation R&D, environmental assessment.**A) OPERATIONAL SCOPE**

This unit can be used to sample solids with particle size less than 0.64 cm (1/4 in.) in diameter, as well as slurries and liquids from pipes fitted with at least 5.08-cm (2-in.) diameters of inports. If a Teflon sampler is used, the maximum temperature range is 250°C. Stainless steel can be used at higher temperatures, but contamination (Ni, Cr, Fe) is added to the sample.

B) INTERFERENCES/LIMITATIONS

Under high temperature conditions where nylon or Teflon cannot be used, the SS collection area can be corroded and contaminate the sample.

C) RECOMMENDED USE AREA

Trace Material sampling (if Teflon parts are used) for engineering evaluation R&D.

5. OPERATIONAL PARAMETERS**A) RANGE** N/A**B) ACCURACY** N/A**C) PRECISION** N/A**6. REAGENTS REQUIRED**

Sample bottles (see 02-01-01).

7. EQUIPMENT REQUIRED

Model RTA Pneumatic Sampler (Quality Control Equipment Corp., Des Moines, Iowa).

8. KEYWORD INDEX: Sampling, solid sampling, pneumatic sampler.**9. CROSS REFERENCE ID NUMBERS** 02-01-01, 02-01-02.**10. REFERENCES****A) PRIMARY SOURCE**

018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurement: Trace Inorganic Materials," TRW Systems Group, EPA Contract Number 68-02-1398, July 19, 1975.

B) BACKGROUND INFORMATION

077 Perry, J.H. (ed.), Chemical Engineers Handbook, 4th ed., McGraw-Hill, New York, 1969.

C) FIELD APPLICATIONS

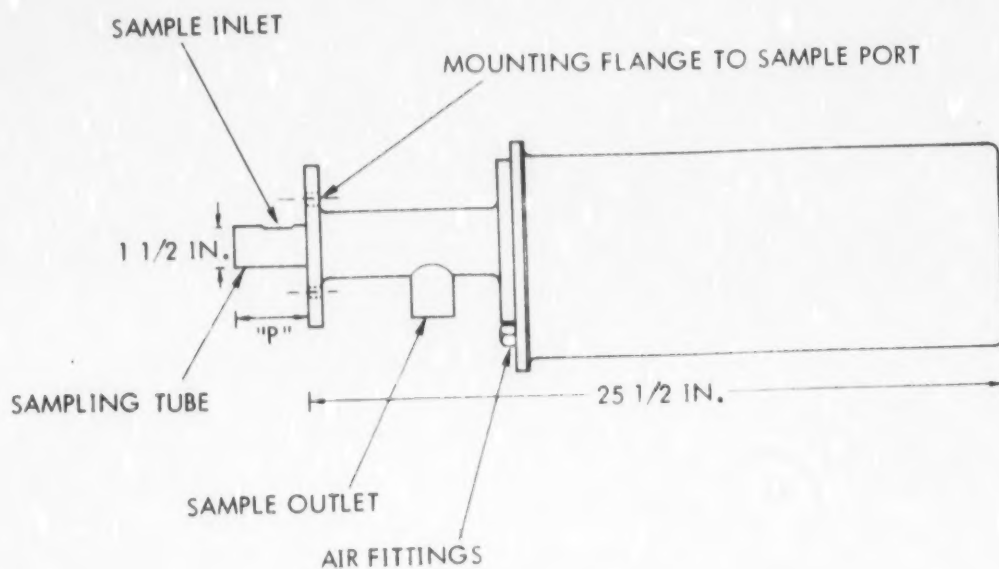


Figure 01-03-01-01A. Pneumatic Sampler Schematic.

2. IDENTIFICATION CODE

01-03-01-02

1. TITLE SAMPLING OF SOLIDS (COAL) USING STANDARD MECHANICAL METHODS

3. ABSTRACT OF METHODOLOGY

When the top size range of the coal and condition of coal preparation are known, a gross sample is obtained; the minimum number of sample increments and their minimum specified weight are shown in Table 01-03-01-02A.

There are two general types of mechanical samples which can be employed for increment-taking: (a) moving samplers, which take a sample of all the stream part of the time; and (b) stationary samplers, which take part of the stream all of the time. In stationary mechanical samplers, the entire stream is continuously fed through the device and stationary cutting edges remove specific fractions. The most common stationary devices are riffles and whistle-pipes. (See 02-01-03-02 for riffle description.)

Moving samplers use cutters which move through the stream for continuous sampling for a given time period. Moving samplers use either cutters which are set on radii of an arc, or cutters with edges parallel to each other and perpendicular to the stream. When sampling characteristics or variances other than top size range and coal preparation are known, the number and weight of increments which need to be taken for each gross sample are calculated using standard formulae. The collected samples are then subsampled by riffling or by manual subdivision. (See 02-01-03-02.)

4. APPLICATION: Environmental assessment.

A) OPERATIONAL SCOPE

Method is applicable to sampling (coal) from plant hoppers, conveyor belts, process stream pipes, etc., and stationary sources such as storage piles, rail cars, or barges. Both mechanically cleaned coals and raw coals can be sampled. See Table 01-03-01-02A for top size ranges.

B) INTERFERENCES/LIMITATIONS

Proper use of methods must reflect a consideration of the physical character of the coal, the number and weight of increments, and the overall precision required.

The system as a whole, including sample cutter, chutes, conveyors, crushers and other devices, should be self-cleaning and non-clogging. One must be aware that sampling devices not designed for trace material sampling can contaminate the sample (does not include teflon or polyethylene).

C) RECOMMENDED USE AREA

This is the recommended environmental assessment procedure for mechanical solid (coal) sampling.

5. OPERATIONAL PARAMETERS

A) RANGE Sampling rates are governed by the specifications and/or limitations of the manual or automatic methods used. (See Table 01-03-01-02A.)

B) ACCURACY The sampling accuracy of $\leq \pm 1/10$ of the ash content of the sample can be attained, based on calculations for general and specific sampling procedures for known sampling characteristics. The accuracy of riffle sampling increases as the ratio of chute width to particle size decreases. Arc-path moving samplers are generally more accurate than straight-line samplers.

C) PRECISION The precision for general and specific sampling procedures based on known sampling characteristics can be $\leq \pm 1/10$ of the average of all ash determinations for 95 out of 100 determinations.

6. REAGENTS REQUIRED

N/A

7. EQUIPMENT REQUIRED

Automatic samplers; riffles or whistle-pipes, arc-path samplers (Snyders, Vezins, etc.); straight-line samplers, metal cans with air-tight lids, or heavy vapor-imperious sealable bags for increment containment; two-section belt divider and riffle splitter.

8. KEYWORD INDEX: Mechanical sampling, solids, increment taking, sample division.

9. CROSS REFERENCE ID NUMBERS 02-01-03-02; 02-02-02-02, 02-02-02-06, 02-02-02-07.

10. REFERENCES

A) PRIMARY SOURCE

- 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2234-68, "Standard Methods for Sampling of Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 357-375.
- 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975, p. 5-3.

B) BACKGROUND INFORMATION

- 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2013-68, "Standard Method of Preparing Coal Samples for Analysis," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 323-336.
- 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D431, "Standard Method for Designating the Size of Coal from Its Sieve Analysis," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 72-73.

C) FIELD APPLICATIONS

- 078 Fujimori, T., and K. Ishikawa, Fuel, 51(2), 120 (1972).

TITLE SAMPLING OF SOLIDS (COAL) USING STANDARD
MECHANICAL METHODS (CONTINUED)

ID NO. 01-03-01-02

Table 01-03-01-02A. Number and Weight of Increments for General Purpose Sampling Procedure^a
(From ASTM, Part 19, D2234-68, 1971, p. 357).

Top Size Range	16 mm (5/8 in.) and under	Over 16 to 50 mm (5/8 to 2 in.) incl.	Over 50 to 150 mm (2 to 6 in.) incl.
Mechanically Cleaned Coal			
Minimum number of increments (1)	15	15	15
Minimum weight of increments, lb	2	6	15
Minimum weight of increments, kg	1	3	7
Raw (Uncleaned Coal) ^b			
Minimum number of increments (1)	15	15	15
Minimum weight of increments, lb	2	6	15
Minimum weight of increments, kg	1	3	7

^aFor coals above 150 mm (6 inches) top size, the sampling procedure should be mutually agreed upon in advance by all parties concerned.

^bIf there is any doubt as to the condition of preparation of the coal (for example, mechanically cleaned coal or raw coal) the number of increments for raw coal shall apply. Similarly, although a coal has been mechanically cleaned, it may still show great variation because of being a blend of two different portions of one seam or a blend of two different seams. In such cases, the number of increments should be as specified for raw (uncleaned) coal.

(1) For quantities up to 1,000 tons (900,000 kg), it is recommended that one gross sample represent the lot. For samples of 1,000 tons or over, several alternative methods are available (see Reference 057).

1. TITLE SOLIDS GRAB SAMPLING (LONG PILE ALTERNATE SHOVEL METHOD)		2. IDENTIFICATION CODE 01-03-02-01
3. ABSTRACT OF METHODOLOGY		
Grab sampling of solids consists in taking small, equal portions at random or regular intervals from heaps or piles, or during loading/unloading or discharge from storage bins. Gross samples are taken for each 250 tons of sample, in quantities shown in Table 01-03-02-01A, in 25-50 equal increments, using a shovel or other similar mechanical means. The entire gross sample is then crushed using jaw crushers, rollers, etc., with crushing sizes indicated in Table 01-03-02-01B. The sample is then mixed and reduced by the long-pile, alternate shovel method, followed by coning and quartering, (e.g., piling the sample into a conical heap, then flattening the cone into a circular cake, followed by marking of the cake into quadrants and taking two opposite quadrants while discarding the remaining two quadrants) as illustrated in Figure 01-03-02-01A. The sample is then ready for shipment to the laboratory. Further subdivision of the sample for analyses can be performed in the laboratory by similar manual methods or by use of riffle samplers (see 02-01-03-02 for details).		
4. APPLICATION: Environmental assessment, engineering evaluation R&D.		
A) OPERATIONAL SCOPE Methods are applicable to any gross load of solid, whether stationary or during loading/unloading operations. B) INTERFERENCES/LIMITATIONS N/Q C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment procedure for the grab sampling of solids (coal, coke, etc.).		
5. OPERATIONAL PARAMETERS		
A) RANGE A gross sample can be taken for each 909,000 kg (1000 tons) or less, according to quantities shown in Table 01-03-02-01B; larger tonnages can also be sampled with pre-determined quantities. B) ACCURACY 10% or better C) PRECISION $\pm 0.5\%$		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
N/A	Shovel, crushing equipment; sample containers (Polyethylene bags).	
8. KEYWORD INDEX: Solids, grab sampling, shovel method.		
9. CROSS REFERENCE ID NUMBERS 02-01-03-02; 02-02-02-02, 02-02-02-07, 02-02-02-08.		
10. REFERENCES		
A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, D346-35, Part 19, "Standard Method of Sampling Coke for Analysis," p. 50-56, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 50-56. 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," EPA Contract No. 68-02-1393, TRW Systems Group, July 1975, n. 5-1. B) BACKGROUND INFORMATION 015 ASTM Committee D-2 and F-7, "Petroleum Products - LPG, Aerospace Materials, Sulfonates, Petrolatum, Wax," 1971 Annual Book of ASTM Standards, Part 18, D270-65, "Sampling Petroleum and Petroleum Products," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 47-71. C) FIELD APPLICATIONS 079 Fieldner, A.C., and W.A. Selvig, "The Determination of Moisture in Coke," U.S. Bureau of Mines Technical Paper No. 148 (1971).		

TITLE SOLIDS GRAB SAMPLING (LONG-PILE ALTERNATE SHOVEL METHOD)
(CONTINUED)

ID NO. 01-03-02-01

Table 01-03-02-01A. Sample Types and Minimum Weights of Gross Samples (Reference 057).

Sample Type	Minimum Weight of Gross Samples, kg (lb)
Run-of-oven, blast-furnace, foundry, water-gas, and any coke containing a range of size of pieces made from uncrushed or coarsely crushed coal**, except coke breeze.	228 (500)*
Run-of-oven, blast-furnace, foundry, water-gas, and any coke containing a range of size of pieces made from crushed coals***, except coke breeze.	114 (250)*
Closely-sized coke made from uncrushed or coarsely crushed coal** free of coke breeze.	114 (250)*
Closely-sized coke made from crushed coal*** free of coke breeze.	57 (125)*
Coke breeze (all passing a 1.27- or 1.90-cm (1/2- or 3/4-in.) square-hole sieve).	57 (125)*

*In case the pulverization of the coal is not known, take quantities designated for coke made from uncrushed or coarsely crushed coal.

**More than 10 percent on a 0.635 cm (1/4-in.) square-hole sieve.

***Not less than 90 percent passing through a 0.635 cm (1/4-in.) square-hole sieve.

Table 01-03-02-01B Weights of Coke Samples with Corresponding Crushing Sizes (Reference 057).

Weight of Sample to be Divided, kg (lb.)	Largest Size of Coke and Impurities Allowable in Sample Before Division, cm. (in.)
114 (250) or over	2.54 (1)
57 (125)	1.90 (3/4)
27 (60)	1.27 (1/2)
14 (30)	0.635 (1/4)

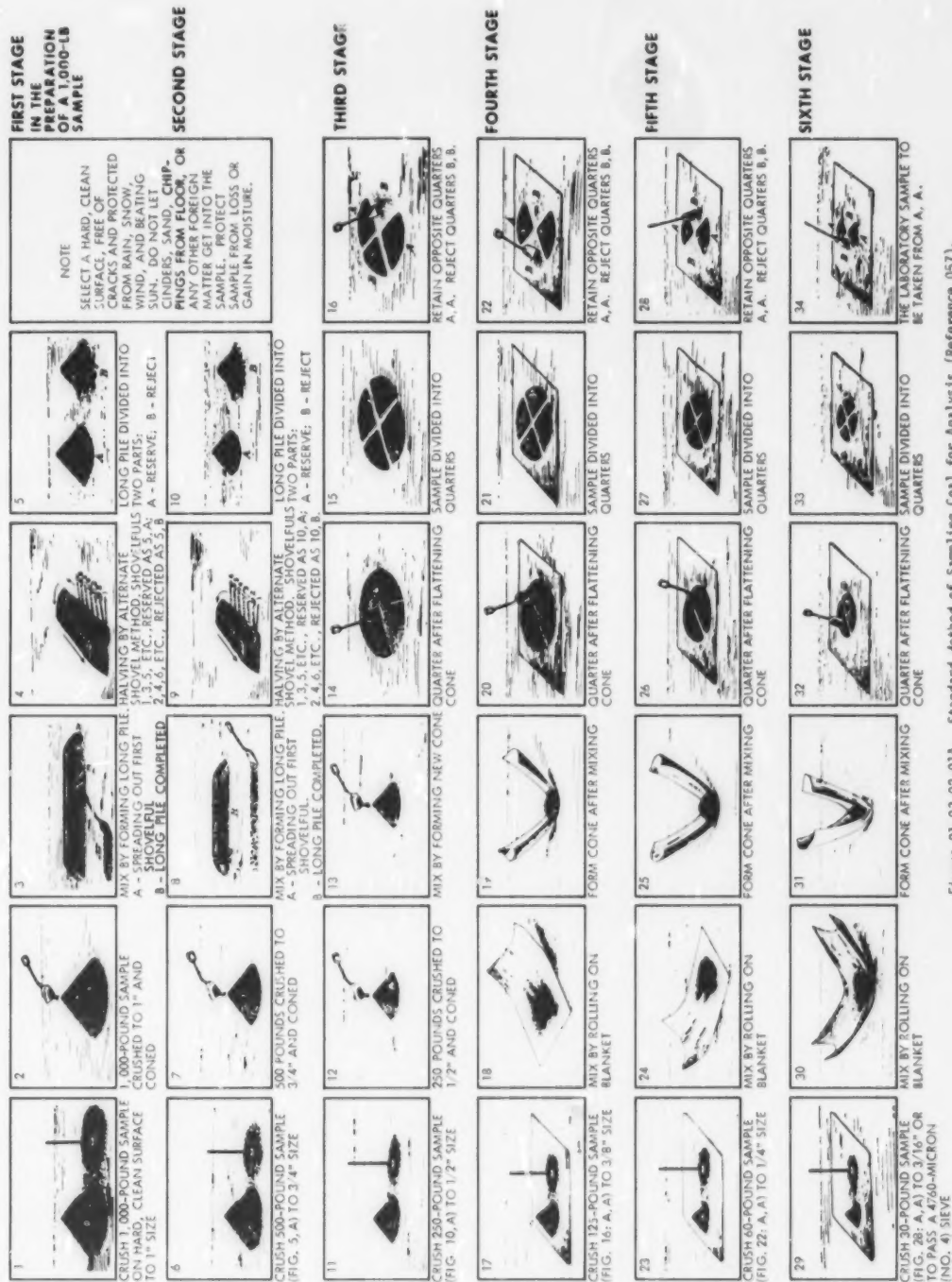


Figure 01-03-02-01A. Standard Method of Sampling Coal for Analysis (Reference 057).

**Table of Contents for 01-04 Sampling for Particulate or
Aerosol in Flue Gas**

01-04-01 Mass Loading Techniques

01-04-01-01 Sampling Flue Gas for Trace Inorganic
Materials

01-04-01-02 Particulate Sampling in Flue Gas Streams for
Non-Trace Element Constituents

01-04-02 Particle Sizing Techniques

01-04-02-01 Particulate Size Sampling in Flue Gas Streams .

01-04-02-02 Level 1 Environmental Assessment Flue Gas
Sampling Train

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APPLICATION MATRIX FOR 01-04 PARTICULATE OR AEROSOL SAMPLING IN FLUE GAS

METHOD	LEVEL 1 ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
01-04-01-01			●
01-04-01-02		●	●
01-04-02-01			●
01-04-02-02	●		

SAMPLING FOR PARTICULATE OR AEROSOL IN FLUE GAS - ID No. 01-04

To obtain a representative particulate sample, general flue gas sampling concepts must be followed. When sampling particles in a flue gas stream, the prime consideration is to sample the gas isokinetically (reference 084). If the sample velocity is below isokinetic conditions, too many large particles will be collected. On the other hand, too many small particles will be collected if the sampling rate is faster than isokinetic conditions. Also, the long axis of the sampling head must be parallel to the direction of the gas flow. In this case, too few large particles will be collected at the sampling head. It is extremely important to avoid collecting size-weighted samples, since it has been shown (references 081, 082, 083) that trace elements show a definite trend in concentration with particle size. Any size weighting of the collected material would affect the concentration of trace elements in a nonrepresentative manner.

The sampling probe itself should be capable of resisting corrosion in the environment of the gas stream. Furthermore, the probe and sampling lines should be heated to 25°C over the stack temperature to prevent condensation of water vapor or other borderline vaporous compounds.

01-04-01 Mass Loading Techniques (Abstracts 01-04-01-01 through 01-04-01-02)

When sampling flue gas for particulates, a decision must be made before the probe is inserted in the stack as to whether trace material or non-trace material is going to be sampled. Furthermore, if trace materials are to be sampled, the specific elements of interest must be known. This decision will have an impact on quality control, equipment design, and laboratory procedures. Obviously, if nontrace materials are to be sampled, the degree of quality control and analytical sensitivity is reduced and thus reagent quality chemicals (02-01-01-01) and acids can be used rather than high purity reagents (02-01-01-06). By the same token if the analyst knows what elements he wishes to collect, even nontrace element trains can be used. For example, if the analyst is interested in As, Se, or Pb, an unlined 316 SS probe could be used rather than the recommended probe

(01-04-01-01), since the common contaminants (Fe, Cr, Ni) will not be measured. However, each case must be decided individually by asking these questions:

- 1) Will the train contribute contamination to the collected sample?
- 2) Will the train modify or irreversibly retain the species or element of interest?
- 3) What precision and accuracy is acceptable?

The size of the sample to be collected is determined by the sensitivity and detection limit of the analytical procedures to be employed and the background levels of the materials of interest. For trace analysis methods, the required element sample sizes range from 10 to 1,000 μg . For a stream containing 60 μg of an element of interest per m^3 , between 0.2 and 15 m^3 (7-420 ft^3) will need to be sampled in order to furnish an adequate sample size. It is clear that in order to acquire this sample in a reasonable period of time (two hours or less) a sampling rate of the order of 0.2 m^3/min (5 ft^3/min) is required.

If one is interested in factor-of-two survey methods (Level 1 environmental assessment) the high volume cyclone train (01-04-02-02) is recommended. If nontrace elements or trace elements other than Fe, Cr, Ni, Mo, Mn, Cu, and V are to be sampled, then the unmodified HVSS train can be used (01-04-01-02). If there is any doubt about compatibility, then the recommended trace material sampling train must be used (01-04-01-01).

01-04-02 Particle Sizing Techniques (Abstracts 01-04-02-01 through 01-04-02-02)

Both in-stack and out-of-stack particle sizing equipment is available. The utility of each approach is mainly dictated by the mass loading and particle size distribution in the gas stream. Out-of-stack sizing methods work where low mass loadings and smaller particle sizes ($<3\mu$) are found. Typically these conditions occur after process control equipment such as electrostatic precipitators or wet scrubbers. Since the particles are small, the chance of collecting particles in the probe and sampling lines is minimized. The Source Assessment Stack Sampler (SASS) (01-04-02-01) uses a series of cyclones ($<10\mu$, $<3\mu$, $<1\mu$) to fractionate the particulates outside of the stack.

The SASS train utilizes a flowrate of 4 cfm so that sampling periods are kept to a minimum. This train is designed to be a survey tool for environmental assessment of pollution sources and is the recommended Level 1 environmental assessment train.

In-stack particle sizing employs cascade impactors. By eliminating the probe and sampling lines, particle loss is essentially eliminated. Many units are on the market, but the MRI unit (01-04-02-01) has the best design and field utility of the commercial units. The MRI impactor is made of aluminum (or 316 SS) and is designed to be placed in the stack (7.62 cm or 3 in. diameter part required). Its high flowrate (up to 1 cfm) and simple design aids in the collection and removal of samples particle.

REFERENCES

- 080 Faith, W.L., and A.A. Atkisson, "Air Pollution," John Wiley, 1972, p. 110.
- 081 Davison, R.L., et al, "Trace Elements in Fly Ash: Dependence of Concentration on Particle Size," Environ. Sci. Tech., 8(13), 1107 (1974).
- 082 Lee, R.E., H. Christ, K. MacLeod and A. Riley, "Concentration and Size of Trace Metal Emissions from a Power Plant, a Steel Plant and a Cotton Gin," Environ. Sci. Tech., 9(7), 643 (1975).
- 083 Lee, R.E., R. Enrione, S. Goranson and G. Morgan, "National Air Surveillance Cascade Impactor Network: II. Size Distribution Measurements of Trace Metal Components," Environ. Sci. Tech., 6(12), 1025 (1972).
- 084 "Methods of Air Sampling and Analysis," American Public Health Association, Washington, D. C., 1972.

1. TITLE SAMPLING FLUE GAS FOR TRACE INORGANIC MATERIALS		2. IDENTIFICATION CODE 01-04-01-01
3. ABSTRACT OF METHODOLOGY This procedure is designed to sample flue gas streams for trace inorganic materials. A standard Aerotherm high volume stack sampler (HVSS) was modified in 3 areas: 1) the probe was lined with an inner removable liner made of Kapton polyimide film to prevent nickel, chromium and other stainless steel elements from contaminating the particulate catch; 2) Gelman Spectrograde type A glass fiber filter was used as the filtering medium and 3) a special oxidative impinger system was developed to sample vaporous elements such as arsenic, mercury, selenium and antimony. The oxidative system consisted of four impingers: one impinger with 3M H₂O₂, two impingers with 0.2 M (NH₄)₂ S₂O₈ plus 0.02 M AgNO₃ and a fourth impinger with Drierite. The impinger nozzles were coated with Teflon to prevent corrosion of the SS components due to the oxidative solutions. Figure 01-04-01-01A shows the Aerotherm high volume stack sampler and Figure 01-04-01-01B is a schematic diagram of a Kapton liner inside the probe tube.		
4. APPLICATION: Engineering evaluation R&D		
A) OPERATIONAL SCOPE This system is designed to operate in a flue gas stream at temperatures up to 450°C. The sampling rate reaches 90 lpm (3 cfm). This system is primarily designed for trace material sampling, but can also be used to collect information on mass loadings.		
B) INTERFERENCES/LIMITATIONS While the Kapton lined probe can operate up to 450°C, Teflon gaskets and coated hardware are not compatible with temperatures much above 270°C. The Aerotherm system is also heavier and larger than low volume Method 5 type samplers. Cleaning the cooling coils can be difficult and time-consuming, and they also show potential for corrosion or impinger sample contamination. While manufacturer specifications indicate that a sampling rate of 180 lpm (6 cfm) is possible, present field sampling has demonstrated that a sampling rate of 90 lpm (3 cfm) is possible with the present configuration.		
C) RECOMMENDED USE AREA This train is recommended as an engineering evaluation R&D trace element sampling train for flue gas streams.		
5. OPERATIONAL PARAMETERS		
A) RANGE The flow rate of the trace material sampling train approaches 90 lpm.		
B) ACCURACY The oxidative impinger system was to be a hundred percent efficient for sampling gaseous mercury.		
C) PRECISION The original Aerotherm HVSS was designed as a Method 5 sampling train; consequently, the built-in precision was better than ±10%.		
6. REAGENTS REQUIRED High purity water, ammonium persulfate, silver nitrate, Drierite, nitric acid, hydrochloric acid.	7. EQUIPMENT REQUIRED Aerotherm high volume stack sampler, Kapton film, bushing inserts, (for a complete list of equipment to perform a 2-point, 20-run gas test, see Ref. 018).	
8. KEYWORD INDEX: Flue gas sampling, trace material sampling.		
9. CROSS REFERENCE ID NUMBERS 01-01-01-05; 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements of Trace Inorganic Materials," TRW Systems Inc., EPA Contract #68-02-1393, July 1975.		
B) BACKGROUND INFORMATION		
C) FIELD APPLICATIONS 025 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Final Report for Measurement Techniques for Inorganic Trace Materials in Control Systems, Streams," TRW Systems Group, EPA Contract #68-02-1393, in press.		

TITLE SAMPLING FLUE GAS FOR TRACE INORGANIC MATERIALS (CONTINUED)

ID NO. 01-04-01-01

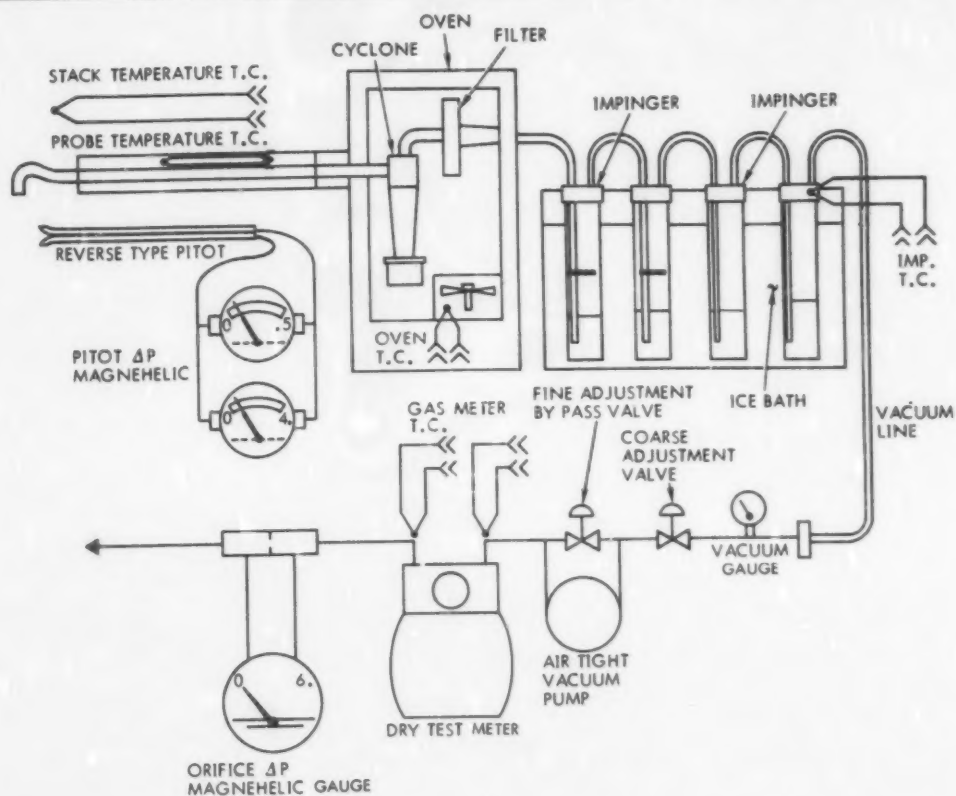


Figure 01-04-01-01A. Aerotherm High Volume Stack Sampler Schematic.

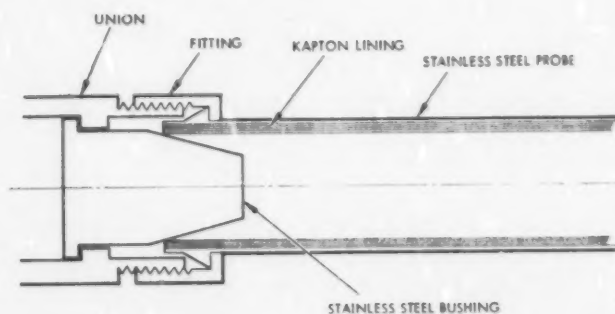


Figure 01-04-01-01B. Schematic Diagram of Kapton Liner Inside Probe Tube.

01-04-01-02

3. ABSTRACT OF METHODOLOGY

4. APPLICATION: Compliance, engineering evaluation R&D

A) OPERATIONAL SCOPE

These systems can be used in most flue gas streams at temperatures up to 250°C. Glass-lined probes are available for extremely corrosive streams and for compliance testing.

B) INTERFERENCES/LIMITATIONS

One must realize that the sampling train can contaminate the collected samples. This awareness will dictate the choice of chemical tests that can be performed so that meaningful data will be generated. For example, the stainless steel components will add Ni, Cr, Fe to the particulate catch, so chemical analyses for these elements would be worthless due to contamination (see 01-04-01-01).

C) RECOMMENDED USE AREA

These sampling trains are recommended for non-trace material sampling for engineering evaluation. When a low volume train (1-2 cfm) is used, then this method conforms to compliance testing for mass loading.

B. OPERATIONAL PARAMETERS

A) RANGE

Up to 250°C and most flue gas environments. Special probes (Quartz and Inconel) are available from manufacturer.

B) ACCURACY

 $\pm 10\%$

C) PRECISION

±10%

REAGENTS REQUIRED

The exact reagents required will be dictated by the goal of the sampling task. See 01-01-01-05 for specific examples.

7. EQUIPMENT REQUIRED

See Table 01-04-01-02A.

KEYWORD INDEX: Sampling, particulate sampling.

9. CROSS REFERENCE ID NUMBERS 01-04-01-01, 01-01-01-01, 02, 03, 04, 05

10. REFERENCES

A) PRIMARY SOURCE

085 Stern, A.C. (ed), "Air Pollution," Academic Press, New York, 2, 1968.

019 U. S. Environmental Protection Agency, Federal Register 36, No. 234, 24938, December 23, 1971.

B) BACKGROUND INFORMATION

026 "Air Sampling," Am. Conf. Gov. Ind. Hyg., 4th ed., Cincinnati, Ohio (1972).

085 "Collaborative Study of Method for the Determination of Particulate Matter Emissions from Stationary Sources (Fossil Fuel-Fired Steam generators)," EPA 650/4-74-021, June 1974.

086 "Collaborative Study of Method for Determination of Particulate Matter Emissions from Stationary Sources (Municipal Incinerators)," EPA 650/4-74-022, April 1974.

087 "Collaborative Study of Method for Determination of Particulate Matter Emissions from Stationary Sources (Portland Cement Plants)," EPA 650/4-74-029, May 1974.

C) FIELD APPLICATIONS

025 Flugal, C.A., M.L. Kraft, C. Lin, R. F. Maddaloni, J.A. Starkovich and C. Zee, "Final Report; Measurement Techniques for Inorganic Trace Materials in Control System Streams," EPA Contract No. 68-02-1393, TRW Defense and Space Systems, Redondo Beach, Ca., 1976.

TITLE PARTICULATE SAMPLING IN FLUE GAS STREAMS FOR NON-TRACE
ELEMENT CONSTITUENTS (CONTINUED)

ID NO. 01-04-01-02

Table 01-04-01-02A.

	Aerotherm HVSS	JOY EPA	Lear-Siegler Pn-100	Rader Pneumatics
Operating Principle	Gas sampled isokinetically and passed through a cyclone, filter and impinger system	Same as Aerotherm HVSS	Same as Aerotherm HVSS	Gas sampled isokinetically and particulate collected in filter
Construction	Stainless steel, teflon, line hose, viton seals, Lexan impingers	Stainless steel, ball joints, glass lines and glass impingers	Stainless steel, ball joints, glass lines and glass impingers	All aluminum with silicone gaskets
Size Cut-offs	> 3 μ cyclone on filter remainder	> 3 μ cyclone (optional) remainder on filter	> 1.5 μ remainder on filter	None available
Air Flowrates	Up to 5 cfm	Up to 3 cfm	Up to 3.5 cfm	Up to 65 cfm
Weight (complete)	~ 80 kg (175 lb)	~ 50 kg (110 lb)	~ 48 kg (105 lb)	12.3 kg (27 lb)

2. IDENTIFICATION CODE

01-04-02-01

1. TITLE PARTICULATE SIZE SAMPLING IN FLUE GAS STREAMS

3. ABSTRACT OF METHODOLOGY

Inertial impactors separate particles on the basis of their aerodynamic size. The sample is drained isokinetically from the source. The sample gas then passes through a series of jet stages. The sample velocity is increased by each stage, thereby imparting an increased inertia to the entrained aerosol. Particles achieving a sufficient inertia to escape the flow stream are impacted on the collection disc located below each jet stage, as shown in Figure 01-04-02-01A. In practice, Mylar liners coated with a grease (typically Apiezon L) are added to prevent particle bounce or re-entrainment of the particles. These liners reduce the weighing problems by eliminating the need to weigh the particles on aluminum or stainless steel collection plates. Table 01-04-02-01A summarizes the characteristics of several commercially available impactors.

4. APPLICATION: Engineering evaluation R&D

A) OPERATIONAL SCOPE

This technique can be used in all flue gas streams and is only limited by the corrosive nature of stream. The MRI unit can be made out of 316 stainless steel. The maximum normal operating temperature is 225°C. The MRI unit does not require a probe, since it is inserted directly into the stack.

B) INTERFERENCES/LIMITATIONS

Except when the Brink unit is used, liquid aerosol streams cannot be sampled. The maximum weight per stage is 10 mg, which makes the chemical analysis difficult.

C) RECOMMENDED USE AREA

The MRI unit is recommended for engineering evaluation R&D for particles in flue gas at low gas loadings. The Brink unit is recommended for liquid aerosol collection and for particles in flue gas at high grain loadings.

5. OPERATIONAL PARAMETERS

A) RANGE

Up to 225°C

B) ACCURACY

N/Q ($\pm 10\%$ estimated)

C) PRECISION

N/Q ($\pm 10\%$ estimated)

6. REAGENTS REQUIRED

Apiezon L, Mylar, high purity water, acetone.

7. EQUIPMENT REQUIRED

MRI Model 1502 (MRI, Altadena, California) or the Brink BMS-11 with deep cups (Monsanto Envirochem, St. Louis, Mo.), pumps (1 cfm flowrate), metering system, probe (only for Brink).

8. KEYWORD INDEX: Sampling, particle sizing, MRI, Brink.

9. CROSS REFERENCE ID NUMBERS See appropriate analytical method.

10. REFERENCES

A) PRIMARY SOURCE

026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments," Cincinnati, Ohio, 4th ed., 1972.

B) BACKGROUND INFORMATION

088 Brink, J.A., E.D. Kennedy and H.S. Yu, "Particle Size Measurements with Cascade Impactors," paper delivered at 65th Annual Meeting of the A.I.C.E., New York, N. Y., November 26-30, 1972.

C) FIELD APPLICATIONS

089 Brink, J.A., "Cascade Impactor for Adiabatic Measurements," *Ind. Eng. Chem.*, **50**(4), 645 (1958).

090 Ensor, D.S., et al, *J. Colloid Interface Sci.*, **38**, 242 (1972).

TITLE PARTICULATE SIZE SAMPLING IN FLUE GAS STREAMS (CONTINUED)

ID NO. 01-04-02-01

Table 01-04-02-01A.

Model Specifications	Brink Deep Cup Impactor	Pollution Control Systems Cascade Impactor, Mark V	Meteorology Research Impactor Model 1503
Operating Principle	Multijet out of stack	Multijet in stack	Multijet in stack
Construction	Stainless steel	Stainless steel	Aluminum
Collection Stages	5 stage	12 stage	7 stage
Range (Microns)	0.25 to 2.5	0.2 to 20	0.3 to 30
Air Flow Rate (cfm)	0.01 to 0.1	0.10 to 1.00	0.1 to 1.0
Backup Filter	Not included	Not included	47 mm glass fiber filter
Nozzle Sizes (mm)	1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 15	1/4, 3/16, 1/8, 1/2	1/8, 3/16, 1/4, 5/16, 3/8, 7/16, 1/2
Collection Efficiency	Practically 100%	Practically 100%	Practically 100%
Dimensions	3.8 cm x 38 cm (1.5 inch x 15 inches)	7.6 cm OD - 35.6 cm (3 inch OD - 14 inch)	6.99 cm OD - 29.2 cm L (2 3/4 inch OD - 11 1/2 inch L)
Weight	2.3 kg (5 lbs)	4.6 kg (10 lbs)	1.6 kg (3.5 lbs) (Al)
Features	Deep cups to collect up to 3 ml of liquid	Minimal blowoff and handling losses	Minimal blowoff and handling losses
Options	BMS-11 is complete sampling kit	Cyclone attachment available	Heating mantle, stainless steel body (#1502)

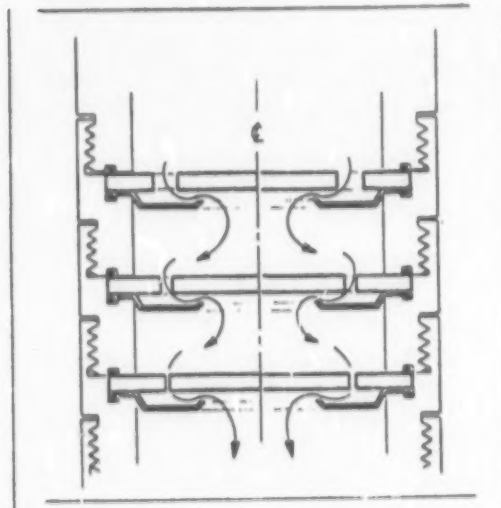


Figure 01-04-02-01A. Schematic of Inertial Impactor.

1. TITLE LEVEL 1 ENVIRONMENTAL ASSESSMENT FLUE GAS SAMPLING TRAIN	2. IDENTIFICATION CODE 01-04-02-02
3. ABSTRACT OF METHODOLOGY In order to sample a flue or duct in such a way that particulate size is measured during the sampling process, a sampling train was designed to collect large quantities of particulate matter, size classified in the ranges of: (a) 10μ, (b) 3μ-10μ, and (c) 1μ to 3μ, with a final filter to provide a sub-micron size cut (Figure 01-04-02-02A). The sampling train consists of a stainless steel probe which enters an oven module containing three cyclones and a filter designed to give the particulate delineation mentioned above. The oven module is followed by an impinger system designed to entrap volatile trace elements (based on 01-01-01-05) with the pumping capacity supplied by one or more high volume vacuum pumps. Necessary pressure, temperature, flow and power conditions are obtained from a main controller. The entire system is represented schematically in Figure 01-04-02-02B. For level 1 environmental assessment, a pseudo isokinetic (single initial isokinetic calculation at start of sampling) sampling will be used to provide survey data on a qualitative, semi-quantitative basis.	
4. APPLICATION: Level 1 environmental assessment.	
A) OPERATIONAL SCOPE This system is designed to operate up to 205°C in flue gas streams.	
B) INTERFERENCES/LIMITATIONS This system is designed to operate unattended and unsequentially if the degree of non-isokinetic sampling varies widely. Probe, cyclones and tubing are made out of Inconel or 316 SS and will contaminate the sample with Fe, Cu, and Ni.	
C) RECOMMENDED USE AREA Level 1 environmental assessment.	
5. OPERATIONAL PARAMETERS	
A) RANGE Up to 700°C	
B) ACCURACY Factor of 2	
C) PRECISION Variable	
6. REAGENTS REQUIRED (NH ₄) ₂ S ₂ O ₈ , AgNO ₃ , High purity H ₂ O, H ₂ O ₂ .	7. EQUIPMENT REQUIRED Environmental Assessment Train (Aerotherm Corp., Mountainview, Ca.).
8. KEYWORD INDEX: Sampling, environmental assessment train.	
9. CROSS REFERENCE ID NUMBERS 01-01-01-05; 02-01-03-03, 04, 05, 06.	
10. REFERENCES	
A) PRIMARY SOURCE 091 Sales Literature, Aerotherm Project 2146 - Source Assessment Sample, Aerotherm Corp., Mountainview, Calif. (Private communication with Fred Moreno, Program Manager, February 19, 1976)	
B) BACKGROUND INFORMATION 092 Chamberlain, A. Grant, T.D. Jones and J. Trost, "Interim Report: Fabrication and Calibration of Series Cyclone Sampling Train," TRW Systems Group, Redondo Beach, California, EPA Contract #68-02-1412, April 1975.	
C) FIELD APPLICATIONS 093 Clausen, J., A. Grant, U. Moore and S. Reynolds, "Interim Report: Field Sampling for Cytotoxicity Test Samples Using a Series Cyclone Sampling Train," TRW Systems Group, Redondo Beach, California, EPA Contract #68-02-1412, October 1975.	

TITLE

LEVEL 1 ENVIRONMENTAL ASSESSMENT FLUE GAS SAMPLING TRAIN (CONTINUED)

ID NO. 01-04-02-02

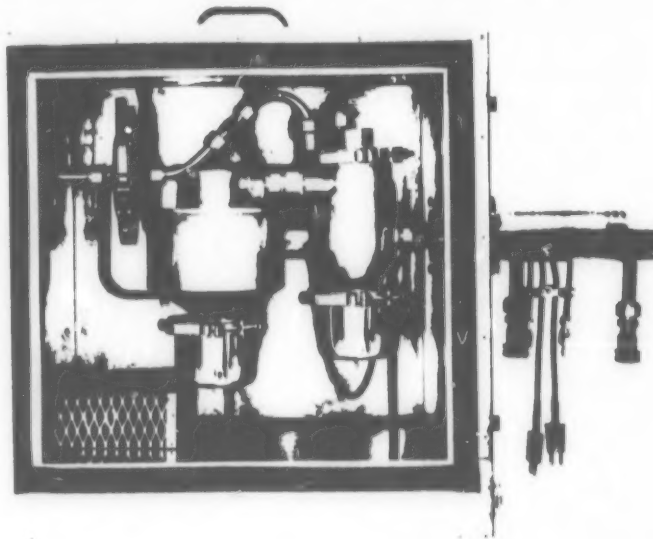


Figure 01-04-02-02A. Photograph of Probe, Cyclones and Filter.

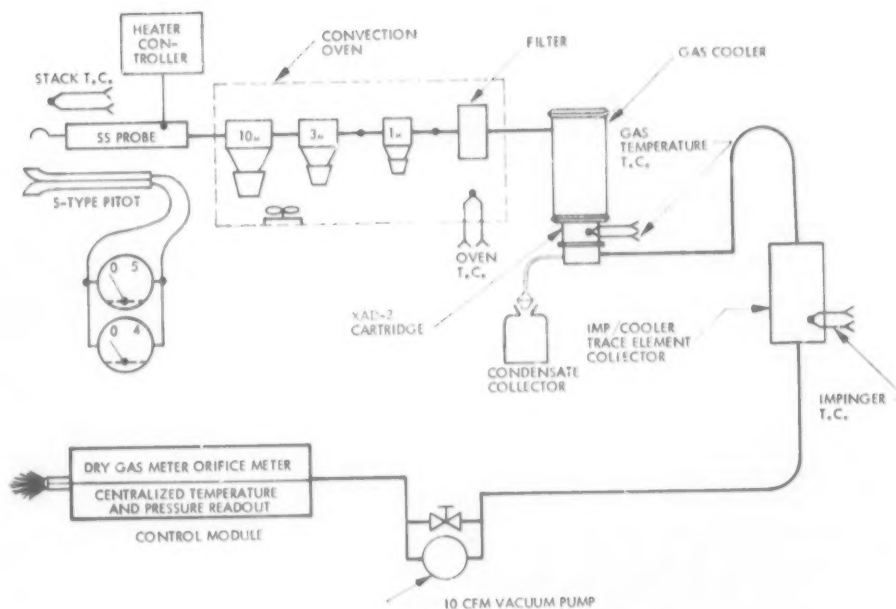


Figure 01-04-02-02 B. System Schematic.

Table of Contents for 01-05 Sampling for Fugitive Gas Emissions

01-05-01 Absorption in Liquids

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Using the Griess-Saltzman Reaction

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01-05-01-03 Sulfur Dioxide Content of the Atmosphere
(West-Gaeke Method)

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01-05-02-01 Fugitive Gas Sampling with Direct Reading
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01-05-02-02 Sampling for Lead in the Atmosphere

01-05-02-03 Impregnated Paper Tape Methods for Determina-
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01-05-02-04 Fugitive Gas Sampling by Adsorption on Solids
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01-05-03 Condensation Techniques

01-05-03-01 Fugitive Gas Sampling by Condensation
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01-05-04 Fugitive Gas Grab Sampling

01-05-04-01 General Fugitive Gas Grab Sampling Techniques

01-05-04-02 Fugitive Gas Grab Sampling Using Plastic Bags

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APPLICATION MATRIX FOR 01-05 SAMPLING FOR FUGITIVE GAS EMISSIONS

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
01-05-01-01	●	●	●
01-05-01-02	●	●	●
01-05-01-03		●	●
01-05-02-01	●		
01-05-02-02			●
01-05-02-03	●		
01-05-02-04	●		●
01-05-03-01			●
01-05-04-01	●		
01-05-04-02	●		

SAMPLING FOR FUGITIVE GAS EMISSION - ID No. 01-05

The differences between flue gas and fugitive gas sampling are more a matter of degree rather than kind. All of the procedure categories for flue gas sampling are applicable to fugitive gas emission sampling, and the reader is directed to 01-01 for a detailed discussion of the problems associated with the different procedure categories. This introduction will discuss the problems associated with fugitive gas sampling, and briefly review the compiled methods.

Sampling for fugitive emissions around a plant will involve sampling vents (atmospheric and high pressure) as well as closed areas surrounding a pollution source (for example, the building housing an open hearth) and boundaries of the plant parameter. All vents to the atmosphere require a means of access as well as a suitable working space for personnel involved in the sampling process. Vent systems generally consist of relief tubes or exit ducts regulated by in-line pressure release valves. Vents of this type are found in holding tanks and storage tanks and are usually released into the air when the tank pressure exceeds the pressure setting of the in-line valve. The velocity of the gases being emitted from vent systems, as well as the time duration of the vent cycle, is directly proportional to: 1) the diameter of the vent tube, 2) the headspace volume of the system being vented, and 3) the pressure setting of the in-line relief valve.

Important considerations in obtaining a representative sample from these sources are:

- The sample must be taken while the vent cycle is in progress. (Cycle periods for individual processes should be known as a result of the pre-test survey).
- The entrance nozzle of the sampling unit should be situated in such a way that a representative sample of the vent effluent is obtained without contamination by ambient air.

Manufacturing, process, or transfer areas either enclosed or open are major sources of fugitive emissions. Depending on the control devices present, the emissions can range from slightly above ambient to near flue gas levels. In all cases, the duration of the sampling period should be integrated with the cyclic nature of the processes.

In obtaining fugitive boundary samples, the perspective is considerably altered with respect to the methods which apply to enclosed structure sampling. Depending on the size of the plant in question, there can be a multitude of isolated sources, each of which contributes to the overall particulate population from different locations in the plant. Naturally, atmospheric mixing will play a role in homogenizing individual emission sources, but certainly not to a reliable degree.

It is recommended that at least four sample points be established at equal distances apart in such a way that if the process under investigation were quartered, each quarter would be represented by one sampler. If the plant is larger, it can be divided into sixths with one sampler for each sixth, and etc., depending on the size of the installation to be sampled. Consequently, in order to obtain reliable data the decision as to the position and number of samplers and the sampling time should be based on:

- 1) The analytical objectives for the acquired samples - If a factor of 2 (level 1) analyses are to be performed, then sampling accuracy can be of the same order (see 01-02 for statistical explanation).
- 2) The total land area of the process in question - Larger plants will require a greater number of sampling points to provide the proper coverage. Too few sampling points in a large plant could conceivably miss sampling point sources (stacks, vents, etc.) due to meteorological conditions.
- 3) The number of emission sources within the system - In order to avoid a biased sample when many emission sources exist in the plant boundaries, the number of sample points should be increased.

- 4) The estimated average fugitive emission concentration - Many situations will require long sampling periods to obtain enough sample for analysis. Thus, the time required to sample will vary inversely with emission concentrations.
- 5) The number of enclosed structures in which particulate levels are expected to be high - Obviously, when more sources of different emissions exist, the network of samplers must also be increased to obtain representative samples.
- 6) Cyclic nature of emissions - All plants will have operations that vary with time. The sample team has the choice to sample for a period of time to overlap the cycles or to time the sampling period to the cycle.

By noting the above considerations, a representative sample of fugitive emissions can be obtained using the methods in this section.

01-05-01 Absorption in Liquids (Abstracts 01-05-01-01 through 01-05-01-03)

The principal inorganic gases that are monitored in fugitive emissions are NO_2 , SO_2 and O_3 (total oxidant). Standard methods for these gases employ trapping the gas in a reactive solution, and reacting the trapped species with a suitable reagent producing a color change.

The Griess-Saltzman reaction (01-05-01-01) is both a sensitive and accurate method of ambient NO_2 monitoring. On the other hand, the current compliance test (KI) for O_3 (01-05-01-02) has been under study (094) to correct the conflicting results sometimes encountered. Included in these recommendations were:

1. Use of constant voltage transformer as part of the ozone generation system.
2. Use of midjet impingers rather than Saltzman bubblers.
3. Use of higher purity KI.
4. Use of air free of H_2O , O_3 , NO , NO_2 , and hydrocarbons.

The West-Gaeke test for SO₂ (01-05-01-03) is widely used for low level SO₂ measurements. Recent tests (094) have shown that temperature control during sampling and storage is necessary to prevent SO₂ loss. Temperature control at 20°C or less is adequate to reduce the daily loss to >1.0%.

01-05-02 Adsorption on Solids (Abstracts 01-05-02-01 through 01-05-02-03)

The main use of solid adsorbents for fugitive emission sampling is for direct reading colorimetric detection tubes (01-05-02-01). Activated charcoal (01-05-02-02) has been used to sample vaporous lead (volatile inorganic and organic lead). Impregnated filter tapes (01-05-02-03) have been used to sample H₂S.

01-05-03 Condensation Techniques

As in flue gas sampling, however, most inorganic gases of interest have too low of a boiling point to use condensation as a routine sampling procedure. The use of condensation techniques for fugitive gas sampling is described in 01-05-03-01.

01-05-04 Fugitive Gas Grab Sampling (Abstracts 01-05-04-01 through 01-05-04-02)

The same gas containers (01-05-04-01) used for stack gas sampling (01-01-04) can be used for fugitive emissions. Where temperature and pressure allow, plastic bags (01-05-04-02) may be used. Plastic bags are especially useful when low concentrations and large samples are required.

REFERENCES

- 094 Personal communication to Ray Maddalone, TRW Systems, from John Clements, Chief of Methods Standardization and Performance Evaluation Branch.

1. TITLE NITROGEN DIOXIDE CONTENT OF THE ATMOSPHERE USING THE GRIESS-SALTZMAN REACTION	2. IDENTIFICATION CODE 01-05-01-01
3. ABSTRACT OF METHODOLOGY	
The gas sample is passed through an absorbing/color-forming reagent of sulfanilic acid, glacial acetic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride (NAD-C1). This reagent solution scrubs the NO₂ from the gas stream and the NO₂ reacts with the NAD-C1 to form a red-violet color. The absorbance of this solution is read at 550 nm.	
4. APPLICATION: Compliance, level 1 environmental assessment, engineering evaluation R&D.	
A) OPERATIONAL SCOPE This method covers the manual determination of nitrogen dioxide in the atmosphere using fritted bubblers. The method is preferred when high sensitivity is needed. For higher concentrations, for automotive exhaust, or for samples relatively high in sulfur dioxide content, other methods should be used (see 01-01-01-02). B) INTERFERENCES/LIMITATIONS The tenfold ratio of sulfur dioxide to nitrogen dioxide produces no effect. A thirtyfold ratio bleaches the color to a slight extent. The addition of 1 percent acetone to the reagent before use retards the fading by forming a temporary addition product with sulfur oxide. Pre-acetone addition permits reading within 4-5 hours without appreciable interferences. A fivefold ratio of ozone to NO₂ will cause a small interference. Peroxyacetylnitrate (PAN) can give a response of approximately 15-35% of an equivalent molar concentration of NO₂. Normal PAN ambient air concentrations are too low to cause any significant error if an evacuated bottle or syringe method is used to sample concentrations above 5 ppm. (Interference from NO due to oxidation is possible.) Note: If strong or oxidizing agents are present, the color should be measured in 1 hour if possible to minimize any loss. C) RECOMMENDED USE AREA Compliance testing of fugitive emissions.	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.005 ppm to about 5 ppm B) ACCURACY N/Q C) PRECISION ±1%	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Sulfanilic acid, glacial acetic acid, N-(1-naphthyl)-ethylenediamine dihydrochloride, nitrate-free water, sodium nitrate.	Glass manometer, fritted rubber (max. pore size of 60µ) flowmeter pump.
8. KEYWORD INDEX: Compliance NO ₂ sampling.	
9. CROSS REFERENCE ID NUMBERS 01-01-01-02.	
10. REFERENCES	
A) PRIMARY SOURCE 013 ASTM, "Standard Method for Tests for Nitrogen Dioxide Content of the Atmosphere (Griess-Saltzman Reaction)," 1974 Annual Book of ASTM Standards, Part 26, p. 317. 380 U.S. Environmental Protection Agency, Title 40, Part 50, Chapter 1, Appendix F, Washington, D. C. B) BACKGROUND INFORMATION 095 Saltzman, B.E., "Colorimetric Micro Determination of Nitrogen Dioxide in the Atmosphere," <u>Anal. Chem.</u>, 26, 1949 (1954). C) FIELD APPLICATIONS 096 Saltzman, B.E., "Preparation and Analysis of Calibrated Low Concentrations of 16 Toxic Gases," <u>Anal. Chem.</u>, 33, 1103 (1961). 097 Shaw, J.E., "The Measurement of Nitrogen Oxide in the Air," <u>Atm. Environ.</u>, 81 (1967).	

2. IDENTIFICATION CODE	
1. TITLE OXIDANT (OZONE) CONTENT OF THE ATMOSPHERE	01-05-01-02
3. ABSTRACT OF METHODOLOGY	
Micro amounts of oxidant (ozone) are collected by absorption in a solution of alkaline potassium iodine. After acidification, the iodine equivalent to the concentration of the oxidant present in the air is determined precisely and rapidly by spectrophotometric measurement of the absorption of the tri-iodide ion at 352 nm.	
4. APPLICATION: Compliance, level 1 environmental assessment, engineering evaluation R&D.	
A) OPERATIONAL SCOPE This method covers the determination of low concentrations of oxidant (ozone) in the atmosphere. The method is not specific for ozone since other oxidants and reducing substances interfere. The interference of sulfur dioxide and nitrogen dioxide can be eliminated during the analysis of the sample. B) INTERFERENCES/LIMITATIONS Oxidizing and reducing substances may interfere with the oxidation of potassium iodide. Sulfur dioxide will not interfere if the absorbed gas is oxidized with hydrogen peroxide and the excess peroxide boiled off before the acid is added. The oxygen of the atmosphere does not oxidize the absorbing solution appreciably. C) RECOMMENDED USE AREA Compliance.	
5. OPERATIONAL PARAMETERS	
A) RANGE The limit for detection of ozone collected by the method described is 1 to 16 ug. For higher concentrations, appropriate dilutions with absorbing solutions must be made. B) ACCURACY N/Q (According to the primary source, no absolute tests using ozone have been completed). C) PRECISION Samples collected in parallel and in the same atmosphere give values that are in good agreement with each other.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Potassium iodide, sodium hydroxide, glacial acetic acid, hydrogen peroxide, iodine, DI water.	PVC tubing, impinger, air flow meter, air pump, spectrophotometer.
8. KEYWORD INDEX: Sampling, ozone sampling.	
9. CROSS REFERENCE ID NUMBERS 02-05-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 053 ASTM, "Standard Method of Tests for Oxidant (Ozone) Content of the Atmosphere," 1974 Annual Book of ASTM Standards, Method D1609-60, Part 26, p. 327. 480 U.S. Environmental Protection Agency, Title 40, Part 50, Chapter 1, Appendix D, Washington, D. C. B) BACKGROUND INFORMATION 098 Smith, R.G., and P. Diamond, "The Micro Determination of Ozone (Preliminary Studies)," <u>Amer. Ind. Hyg. Assoc. Quart.</u>, 13, 235 (1952). C) FIELD APPLICATIONS	

1. TITLE SULFUR DIOXIDE CONTENT OF THE ATMOSPHERE (WEST-GAEKE METHOD)		2. IDENTIFICATION CODE 01-05-01-03
3. ABSTRACT OF METHODOLOGY A measured air sample containing sulfur dioxide is absorbed in 10 ml 0.4 M sodium or potassium tetrachloromercurate (TCM) using a midget impinger. This procedure stabilizes the SO₂ as a dichlorosulfitomercurate complex which resists air oxidation. Ethylenediaminetetraacetic acid disodium salt is added to the 0.4 M TCM to prevent heavy metals from oxidizing the SO₂ prior to stabilization as the dichlorosulfitomercurate complex. After absorption, any ozone in solution is allowed to decay. The TCM solution is first treated with sulfamic acid to oxidize any nitrite formed from the absorption of oxides of nitrogen. Formaldehyde and acid-bleached pararosaniline (containing phosphoric acid to control pH) are added next to the TCM. These reagents react with the sulfite in the dichlorodisulfitomercurate complex to form an intensely colored compound, pararosaniline methyl sulfonic acid, whose color at a pH of 1.6 and 548 nm is directly related to the SO₂ (SO₃²⁻) in the TCM.		
4. APPLICATION: Compliance, engineering evaluation R&D.		
A) OPERATIONAL SCOPE This method is applicable to collecting and measuring SO ₂ at low levels from fugitive emissions.		
B) INTERFERENCES/LIMITATIONS The interference by oxides of nitrogen are eliminated by sulfamic acid, the ozone by time delay, and the heavy metals by EDTA and phosphoric acid. At least 60 ug of Fe (III), 10 ug of Mn (II), and 10 ug of Cr (III) in 10 ml of absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 ug of Cu (II) and 22 ug of V (V).		
C) RECOMMENDED USE AREA This is the recommended compliance method for sulfur dioxide in fugitive emissions.		
5. OPERATIONAL PARAMETERS		
A) RANGE 0.003 to 5 ppm SO ₂ .		
B) ACCURACY N/Q (±15 percent estimated).		
C) PRECISION ±4.6 percent.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Potassium chloride, mercury (II) chloride, sulfamic acid, 1-butanol, sodium acetate, EDTA, hydrochloric acid, phosphoric acid, pararosaniline hydrochloride, formaldehyde, iodine, starch, sodium sulfite (or SO ₂ permeation tube for calibration purposes).		Midget impingers (or liquid absorption systems), flowmeter, manometer, UV/VIS spectrometer, teflon tubing.
8. KEYWORD INDEX: Air sampling, SO ₂ absorption.		
9. CROSS REFERENCE ID NUMBERS 02-05-02-03; 01-01-01-01.		
10. REFERENCES		
A) PRIMARY SOURCE 053 ASTM, "Tentative Method of Test for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)," 1974 Annual Book of ASTM Standards, Part 26, Method D2914-70T, p. 579. 480 U. S. Environmental Protection Agency, Title 40, Part 50, Chapter 1, Appendix A, Washington, D. C.		
B) BACKGROUND INFORMATION 099 West, P.W., and G.C. Gaeke, "Fixation of Sulfur Dioxide as Sulfite Mercurate (II) and Subsequent Colorimetric Determination," <u>Anal. Chem.</u> , 28 , 1816 (1956). 100 Pate, J.B., B.E. Ammons, J.P. Lodge and G.A. Swanson, "Nitrite Interference in Spectrophotometric Determination of Atmospheric Sulfur Dioxide," <u>Anal. Chem.</u> , 39 , 942 (1965). 101 Scaringelli, F.P., S.A. Frey and B. E. Saltzman, "Evaluation of Teflon Permeation Tubes for Use with Sulfur Dioxide," <u>Am. Ind. Hyg. Assoc. J.</u> , 28 , 260 (1967).		
C) FIELD APPLICATIONS 102 Scaringelli, F.P., B.E. Saltzman and S.A. Frey, "Spectrophotometric Determination of Atmospheric Sulfur Dioxide," <u>Anal. Chem.</u> , 39 , 1709 (1967).		

1. TITLE FUGITIVE GAS SAMPLING WITH DIRECT READING COLORIMETRIC DETECTION TUBES		2. IDENTIFICATION CODE 01-05-02-01
3. ABSTRACT OF METHODOLOGY		
Gas detection tubes are narrow glass cylinders containing a solid absorbent impregnated with a chemical reagent. This reagent turns color as a known volume of the gas is pulled through the tube by means of a small hand pump. The length of the stain on the absorbing material is directly related to the concentration of the species in the gas sample. The scale corresponding to the concentration may be printed either directly on the tube or on a chart which is provided with the detection tubes. In some cases, the stains change with time, and thus a reading should be made immediately after sampling. If the detector tubes are to be kept as evidence, it is recommended that the open ends be sealed.		
4. APPLICATION: Environmental assessment.		
A) OPERATIONAL SCOPE These tubes can be used to sample fugitive emissions for many varieties of gases. Table 01-01-02-01A lists typical gases that can be sampled by the Kitagawa gas detection tubes. Detection tubes are also available for many organic gases. Normally, the tubes are designed to sample gases in a temperature range from 0 to 50°C. It is also assumed that the sampling pressure is 760 millimeters of mercury. If the conditions deviate widely from these conditions, the appropriate correction factors derived from the gas law are available for a particular pressure. (See 01-01-02-01 for information on using detection tubes to sample flue gas streams.) B) INTERFERENCES/LIMITATIONS Experience in sampling known concentrations of gas is of great value in training the operator to know whether to measure the length up to the beginning or the end of the stained front or what portion of an irregular shaped stain to use as a limit. Care must be taken to see that pump valves and connections are maintained and that all connections are leak-proof. In all cases, one must be completely aware of possible interferences to the measurement of the gas of interest. These interferences are listed in Table 01-01-02-01A. C) RECOMMENDED USE AREA This is the recommended level I environmental assessment fugitive emission survey gas analysis technique.		
5. OPERATIONAL PARAMETERS		
A) RANGE See Table 01-01-02-01A for the gas of interest. B) ACCURACY The tube reading deviates from the true value by +25% at most. For many tubes with scales, the deviation is less than +10%. C) PRECISION Precision will depend on the operator. Experience is needed to obtain accurate and precise measurements.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Detector tubes (several possible sources are available: National Mine Service Co., Pittsburgh, Pa.; Unico Environmental Instruments Corp., Fall River, Mass.).	Hand pump (Note: The detector tubes normally come in a complete kit containing hand pump and any equipment necessary to sample gas using the tubes.).	
B. KEYWORD INDEX: Sampling, detector tubes.		
9. CROSS REFERENCE ID NUMBERS 01-01-02-01.		
10. REFERENCES		
A) PRIMARY SOURCE 026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments," Cincinnati, Ohio, 1972, p. S-1 through S-50. B) BACKGROUND INFORMATION Table 01-01-02-01A C) FIELD APPLICATIONS Table 01-01-02-01A		

1. TITLE SAMPLING FOR LEAD IN THE ATMOSPHERE	2. IDENTIFICATION CODE 01-06-02-02
3. ABSTRACT OF METHODOLOGY	
The sample is drawn through a sampling train consisting of a 0.45 μ membrane filter or its equivalent and then through a sampling tube containing activated carbon. A sample of 150-200 ms is collected. (See 02-01-01-01 for analysis techniques.) This sampling train separates particulate lead and vaporous lead. Particulate lead is that sample collected on an 0.45 μ filter. Vaporous lead is that which passes through the 0.45 μ membrane filter, and includes various tetraethyllead compounds or their partially decomposed products or both.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE This method is primarily intended for measuring weekly averages of: a) vaporous lead in fugitive emissions at concentrations below 0.5 $\mu\text{g}/\text{m}^3$ and b) the particulate lead in fugitive emissions at concentrations of 0.01 μg of lead per m^3 of air. B) INTERFERENCES/LIMITATIONS Particulate lead is an ever-present interference when measuring vaporous lead in ambient air. It must be excluded from the activated carbon absorber by use of highly efficient filter and filter holder. Leak-proof gas tubing connections and proper sealing of the filter in the filter holder are necessary to prevent leaks of nonfiltered air. The particulate lead in air entering the carbon absorber must be reduced to less than 0.01 μg of lead per m^3 of air to avoid a positive interference in measuring vaporous lead. C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D sampling method for vaporous lead in the atmosphere.	
5. OPERATIONAL PARAMETERS	
A) RANGE Less than 0.5 $\mu\text{g}/\text{m}^3$ vaporous lead and between 0.01 to 10 $\mu\text{g}/\text{m}^3$ particulate lead. B) ACCURACY $\pm 10\%$ (estimated). C) PRECISION $\pm 10\%$ (estimated).	
6. REAGENTS REQUIRED Activated charcoal.	7. EQUIPMENT REQUIRED Filters (millipore membrane filter, Type HA or equivalent), filter holder, gas meter, vacuum pump.
8. KEYWORD INDEX: Sampling, particulate lead, vaporous lead.	
9. CROSS REFERENCE ID NUMBERS 02-02-01-01.	
10. REFERENCES	
A) PRIMARY SOURCE 053 ASTM, "Lead in the Atmosphere by Colorimetric Dithizone Procedure," 1974 Annual Book of ASTM Standards, Part 26, D3112-72-T, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 633. B) BACKGROUND INFORMATION 103 Snyder, L.J., <u>Anal. Chem.</u>, 39, 591 (1967). 104 Snyder, L.J., <u>Anal. Chem.</u>, 19, 684 (1947). 105 Henderson, F.R., and L.J. Snyder, <u>Anal. Chem.</u>, 31, 2113 (1959). C) FIELD APPLICATIONS	

1. TITLE IMPREGNATED PAPER TAPE METHODS FOR DETERMINATION OF HYDROGEN SULFIDE IN AIR	2. IDENTIFICATION CODE 01-05-02-03																								
3. ABSTRACT OF METHODOLOGY Method involves collection of H ₂ S on impregnated paper tapes under controlled conditions (see Table 01-05-02-03A). Tape reagents include silver nitrate, silver cyanide, mercuric chloride and lead acetate. The hydrogen sulfide reacts with the tape reagent to form a precipitate (silver sulfide, mercuric sulfide and lead sulfide) which produces a visible coloration on the paper tape. The optical densities of the metal sulfide spots are then used as measures of the H ₂ S concentration, using the equation: $\text{conc. H}_2\text{S (ppm)} = KAD/V$, where K is a constant which depends on the optical design of the densitometer, A is the area of the sulfide spot, D is the diffuse optical density, and V is the sample volume.																									
Table 01-05-02-03A. Experimental Conditions Required for Hydrogen Sulfide Determinations Using Impregnated Tapes (Reference 106).																									
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">Chemical Impregnant</th> <th style="width: 20%;">Optimal Flow Rate (liters/min/in²)</th> <th style="width: 20%;">Exposure to Light</th> <th style="width: 35%;">Other Requirements</th> </tr> </thead> <tbody> <tr> <td>AgNO₃</td> <td>< 60</td> <td>Exclude light</td> <td>Avoid temperatures > 40°C; avoid high flow rates at < 10% RH(1); hold tape by edges only.</td> </tr> <tr> <td>HgCl₂</td> <td>< 15</td> <td>—</td> <td>Redevelop spots with NH₃ when necessary; avoid high flow rates at < 10% RH.</td> </tr> <tr> <td>Ag(CN)₂⁻</td> <td>< 10</td> <td>—</td> <td>RH > 20%; avoid storage > 3 months.</td> </tr> <tr> <td>Pb(OAc)₂</td> <td>< 5</td> <td>Exclude light</td> <td>RH > 20%; exclude SO₂ levels equal to H₂S levels; maintain acidic impregnating solutions. Least useful.</td> </tr> <tr> <td colspan="4">(1) Relative Humidity (RH)</td> </tr> </tbody> </table>		Chemical Impregnant	Optimal Flow Rate (liters/min/in ²)	Exposure to Light	Other Requirements	AgNO ₃	< 60	Exclude light	Avoid temperatures > 40°C; avoid high flow rates at < 10% RH(1); hold tape by edges only.	HgCl ₂	< 15	—	Redevelop spots with NH ₃ when necessary; avoid high flow rates at < 10% RH.	Ag(CN) ₂ ⁻	< 10	—	RH > 20%; avoid storage > 3 months.	Pb(OAc) ₂	< 5	Exclude light	RH > 20%; exclude SO ₂ levels equal to H ₂ S levels; maintain acidic impregnating solutions. Least useful.	(1) Relative Humidity (RH)			
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Pb(OAc) ₂	< 5	Exclude light	RH > 20%; exclude SO ₂ levels equal to H ₂ S levels; maintain acidic impregnating solutions. Least useful.																						
(1) Relative Humidity (RH)																									
4. APPLICATION: Environmental assessment.																									
A) OPERATIONAL SCOPE Method is applicable to gas grab sampling of flue gas, fugitive gas, emissions, etc., up to approximately 100°C (212°F).																									
B) INTERFERENCES/LIMITATIONS Moisture must be maintained in order to achieve quantitative collection of H ₂ S. Impregnation of the tapes with glycerol will eliminate this interference. Other precautions necessary for good quantitative analysis are shown in Table 01-05-02-03A. Silver nitrate is the most sensitive and specific determination; lead acetate tapes are the least desirable, but are suitable for semi-quantitative determinations.																									
C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment method for determination of hydrogen sulfide in gaseous effluents.																									
5. OPERATIONAL PARAMETERS																									
A) RANGE 0.001 to 50 ppm using silver nitrate tapes.																									
B) ACCURACY 85% or better.																									
C) PRECISION Reproducibility achieved for air containing 0.008 ppm H ₂ S at flow rates and sampling times giving optical densities of ±0.005 were ±8%, ±6%, ±12%, ±15% for AgNO ₃ , HgCl ₂ , Ag(CN) ₂ ⁻ , and Pb(OAc) ₂ tapes, respectively.																									
6. REAGENTS REQUIRED Silver nitrate, potassium cyanide, mercuric chloride, lead acetate, nitric acid, glycerol.	7. EQUIPMENT REQUIRED Glass fiber tapes (Gelman Type A) or Whatman No. 1, 4 or 41 paper tapes; automatic paper tape sampler (Gelman, Bendix); densitometer.																								
8. KEYWORD INDEX: Hydrogen sulfide, gas grab sampling, impregnated paper tapes.																									
9. CROSS REFERENCE ID NUMBERS 01-01-04-01; 01-05-04-01; 02-03; 01-01-01-07																									
10. REFERENCES																									
A) PRIMARY SOURCE 106 Matusch, D.F.S., J.R. Sewell and R.L. Tanner, "Determination of Hydrogen Sulfide in Air - An Assessment of Impregnated Paper Tape Methods," <i>Anal. Chem.</i> 46(3), 411, March 1974.																									
B) BACKGROUND INFORMATION 015 ASTM Committee D-2 and F-7, "Petroleum Products," 1971 Annual Book of ASTM Standards, Part 18, D2420-66, "Standard Method of Test for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases, (Lead Acetate Method)," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 504-505. 107 ASTM Committee D-1, D-16 and D-17, "Paint, Varnish, Lacquer and Related Products," Part 20, D953-47, "Standard Method of Test for Color, and Hydrogen Sulfide and Sulfur Dioxide Content (Qualitative) of Industrial Aromatic Hydrocarbons," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 438-9.																									
C) FIELD APPLICATIONS 108 H.P. Sanderson, M. Katz and R. Thomas, <i>J. Air Pollut. Control. Assoc.</i> , 16, 328 (1966). 109 A.F. Smith, D.E. Cunningham and D.A. Jenkins, <i>J. Appl. Chem.</i> , 11, 317 (1961). 110 D.F.S. Matusch, <i>Clean Air</i> , 4, 69 (1970). 111 Wohlers, H.C., and M. Feldstein, <i>J. Air Pollut. Control Assoc.</i> , 16, 19 (1966).																									

2. IDENTIFICATION CODE

01-05-02-04

1. TITLE FUGITIVE GAS SAMPLING BY ADSORPTION ON SOLIDS (CARBON, SILICA)

3. ABSTRACT OF METHODOLOGY

Table 01-05-02-04A gives retentivities (practical sorption capacities) of activated carbon for some commonly encountered gases. To collect samples of vapors having retentivity of over 5%, a metered air stream must be passed through a carbon bed of 3/4 inch (19 mm) thickness, with contact time of 1/3 seconds or more [1 1/2 in. thickness (3.81 cm) and 2/3 seconds for 5% or less retentivity]. Table 01-05-02-04B gives minimum specifications for activated carbon for sampling heavy gases boiling above 0°C. Adsorbed gases and vapors may be desorbed from activated carbon by: 1) displacement by superheated steam, and 2) heating under vacuum, with distilling into cold traps. (See 01-01-02-02)

The adsorbent can also be impregnated with suitable reagents (e.g., lead acetate for H₂S, sulfuric acid for NH₃) in order to facilitate sorption of low boiling vapors. (See 01-05-02-03)

4. APPLICATION: Engineering Evaluation R&D, environmental assessment.

A) OPERATIONAL SCOPE

Method is applicable to low boiling vapors (-100 to 0°C) with critical temperatures between 0 and 150°C and to heavier vapors (boiling above 0°C); applicable streams include product gas, process vents, and ambient air. See Table 01-05-02-04A for list of applicable samples.

B) INTERFERENCES/LIMITATIONS

Gases having boiling points below -150°C and critical temperature below -50°C (-58°F) (e.g., H₂, H₂, O₂, CO, CH₄) are nonadsorbable at ordinary temperatures.

C) RECOMMENDED USE AREA

This is the recommended engineering evaluation R&D method for fugitive gas sampling by adsorption on solids, such as carbon or silica.

5. OPERATIONAL PARAMETERS

- A) **RANGE** Range is generally dependent upon size and design of adsorbers, desorption apparatus, etc. Sensitivity of carbon or silica for hydrogen sulfide can be improved by using lead acetate or silver cyanide impregnants; for ammonia, sulfuric acid; for arsine, copper and silver oxidation catalysts. (See 01-05-02-01)
- B) **ACCURACY** N/Q
- C) **PRECISION** ±10%

6. REAGENTS REQUIRED

Activated carbon (see Table 01-05-02-04B for specifications) or silica; reagents for impregnation of adsorbent.

7. EQUIPMENT REQUIRED

Adsorber; blower apparatus, superheated steam or vacuum desorption apparatus, consisting of ice-salt, dry ice and liquid nitrogen traps connected in series.

8. KEYWORD INDEX: Fugitive gas sampling, adsorption on solids, activated carbon, silica gel.

9. CROSS REFERENCE ID NUMBERS 01-05-02-03, 01-05-04-01; 01-01-02-02; 02-03-02; 01-05-02-01

10. REFERENCES

- A) **PRIMARY SOURCE**
 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1605-60, "Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 349-370.
- B) **BACKGROUND INFORMATION**
 026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments for Evaluation of Atmospheric Contaminants," Cincinnati, 4th ed., 1972, p. R-4 through R-6.
- C) **FIELD APPLICATIONS**
 112 White, L.D., R. Kupel, P. Hauer and D. Taylor, Industrial Hygiene News Report, 12(7), July 1969.

TITLE FUGITIVE GAS SAMPLING BY ADSORPTION ON SOLIDS (CARBON, SILICA) (CONTINUED)

ID NO. 01-05-02-04

Table 01-05-02-04A. Retentivity of Vapors by Activated Carbon (Reference 024) (Percentage by Weight Retained in a Dry Air Stream at 20°C, 760 torr).

Substance	Formula	Molecular Weight	Normal Boiling Point, Deg C at 760 torr	Approximate Retentivity, Percent at 20°C and 760 torr	Characteristics
Ammonia	NH ₃	17.0	-33	negligible	refrigerant
Bromine	Br ₂	159.8	59	40 (dry)	organic synthesis
Chlorine	Cl ₂	70.9	-34	15 (dry)	—
Hydrogen bromide	HBr	80.9	-67	8	strong acid
Hydrogen chloride	HCl	36.5	-84	4	strong acid
Hydrogen fluoride	HF	20.0	19	8	strong acid
Hydrogen iodide	HI	127.9	-35.4 (4 atm)	15	strong acid
Hydrogen sulfide	H ₂ S	34.1	-62	3 (dry)	oxidizes to increase retentivity
Iodine	I ₂	253.8	183	40	antiseptic
Nitric acid	HNO ₃	63.0	86	20	oxidizing acid
Nitrogen dioxide	NO ₂	46.0	21	10	hydrolyzes to increase retentivity
Ozone	O ₃	48.0	-112	decomposes to oxygen	generated by electrical discharge
Sulfur dioxide	SO ₂	64.1	-10	10 (dry)	oxidizes to sulfur trioxide; common in city atmospheres
Sulfur trioxide	SO ₃	80.1	45	15 (dry)	hydrolyzes to sulfuric acid
Sulfuric acid	H ₂ SO ₄	98.1	330	30	—
Water	H ₂ O	18.0	100	none	—

Table 01-05-02-04B. Specifications for Air-Purification Activated Carbon (Reference 024).

Property	Specification
Activity for CCl ₄ ^a	at least 50 percent
Retentivity for CCl ₄ ^b	at least 30 percent
Apparent density	at least 0.42 g/ml
Hardness (ball abrasion) ^c	at least 80 percent
Particle size	passing on No. 6 (3.35-mm) sieve retained on No. 14 (1.40-mm) sieve

^aMaximum saturation of carbon at 20°C and 760 mm, in an air stream equilibrated with CCl₄ at 0°C.

^bMaximum weight of adsorbed CCl₄ retained by carbon on exposure to pure air at 20°C and 760 mm.

^cPercentage of carbon passing a No. 6 (3.35-mm) sieve and largely retained on a No. 8 (2.36-mm) sieve, that remains on a No. 14 (1.40-mm) sieve after vibrating with 30 steel balls of 0.25 to 0.37 in. in diameter/50 g of carbon, for 30 min.

2. IDENTIFICATION CODE

01-05-03-01

1. TITLE FUGITIVE GAS SAMPLING BY CONDENSATION TECHNIQUES**3. ABSTRACT OF METHODOLOGY**

Sample collection by condensation involves drawing the sample through condensers or U-tube traps which have been cooled below the boiling point of the gas or vapor.

A representative list of refrigerants is given in Table 01-05-03-01A. Table 01-05-03-01B gives vapor pressure data for several common gases. The vapor pressure of the trapped gases should be 1 torr or lower at trap temperatures. The proper refrigerant is thus selected accordingly.

A typical condensation trap is a glass sampling tube having inlet and outlet ports. The trap may be used as a flask for isothermal distillation at progressively higher temperatures. A U-shaped trap which can be set in a Dewar flask can also be used for collection of gas by condensation.

Table 01-05-03-01A. Refrigerant Temperatures (Reference 024).

Refrigerant System	Temperature, deg C
O ₂ (liquid) = O ₂ (gas)	-183.0
CS ₂ (solid) = CS ₂ (liquid)	-118.5
CO ₂ (solid) = CO ₂ (gas)	- 78.5
NH ₃ (liquid) = NH ₃ (gas)	- 33.4
H ₂ O (solid) = H ₂ O (liquid)	0

4. APPLICATION: Engineering evaluation R&D.**A) OPERATIONAL SCOPE**

The method is applicable to all gases having vapor pressures of ≥ 1 mm at liquid oxygen or higher temperatures. Sampleable streams include product gas, process vents and ambient air.

B) INTERFERENCES/LIMITATIONS

The formation of condensation mists can reduce the equipment collection efficiency; these can be removed by a simple filter (glass wool plug).

The main disadvantage of the condensation technique is the cumbersome nature of the equipment, which also requires frequent attention. The collected sample must be maintained at low temperatures prior to analysis.

C) RECOMMENDED USE AREA

This method is applicable as an engineering evaluation R&D fugitive gas sampling method.

5. OPERATIONAL PARAMETERS

- A) RANGE** Collection range depends on availability of suitable refrigerants for the sampled vapors; sampling rate depends on capability of aspirator, pump, etc.
- B) ACCURACY** 10% or better.
- C) PRECISION** $\pm 10\%$

6. REAGENTS REQUIRED

See Table 01-05-03-01A for listing of suitable refrigerants.

7. EQUIPMENT REQUIRED

Condensation apparatus (Figure 01-05-03-01A); glass wool plug aspirators or pumps to facilitate drawing the sample through the apparatus (see 01-05-04-01).

8. KEYWORD INDEX: Fugitive gas sampling, condensation.**9. CROSS REFERENCE ID NUMBERS** 01-01-03-02, 01-05-04-01; 02-02; 02-03.**10. REFERENCES****A) PRIMARY SOURCE**

024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, D1605-60, Part 23, "Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 349-370.

B) BACKGROUND INFORMATION

026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments for Evaluation of Atmospheric Contaminants," 4th ed., 1972, p. R-3 through R-4, R-12 and R-13.

C) FIELD APPLICATIONS

113 Sanderson, T.T., "Vacuum Manipulation of Volatile Compounds," Appendix, Table XVII, New York, J. Wiley and Sons, Inc., 1948.

114 Shepherd, H., et al, Anal. Chem. ANCHA, Vol. 23, p. 1431, 1951.

TITLE FUGITIVE GAS SAMPLING BY CONDENSATION TECHNIQUES (CONTINUED)

ID NO. 01-05-03-01

Table 01-05-03-01B. Properties of Some Gaseous Atmospheric Contaminants (Reference 024).

Substance	Molecular Wt	Boiling Point, deg C	Freezing Point, deg C	Ordinary State	Vapor Pressure, torr ^a					
					20°C	Ice	NH ₃ -33.4°C	CO ₂ -78.5°C	CS ₂ -111.8°C	O ₂ -183°C
Ammonia	17.0	-33.4	-77.7	vapor	8.46 atm	4.2 atm	1 atm	44.0 (solid)	0.6 (solid)	...
Arsine	77.9	-55	-113.5	vapor	15.0 atm	8.4 atm	2.8 atm	336.0	36.0	0.2
Carbon disulfide	76.1	46.3	-111.8	liquid	295.0	127.0	21.0	0.6	...	...
Chlorine	70.9	-33.8	-102	vapor	6.6 atm	3.7 atm	1 atm	62.0	2.5 (solid)	...
Hydrogen chloride	36.5	-84	-112	vapor	41.6 atm	25.5 atm	9 atm	1.3 atm	120.0	0.8
Hydrogen sulfide	34.1	-61.0	-82.9	vapor	17.7 atm	10.2 atm	3.6 atm	259.0	16.0 (solid)	0.1 (solid)
Ozone	48	-112	-251	gas	...	...	...	...	1 atm	0.17
Sulfur dioxide	64.1	-10.0	-72.7	vapor	3.2 atm	1.5 atm	225	8.4 (solid)	...	...

^a In torr, unless otherwise stated. Vapor pressures are referred to refrigerant temperatures of Table 01-05-03-01A.

1. TITLE GENERAL FUGITIVE GAS GRAB SAMPLING TECHNIQUES		2. IDENTIFICATION CODE 01-05-04-01
3. ABSTRACT OF METHODOLOGY		
Fugitive gas emissions may be collected by gas or liquid displacement techniques using evacuated containers, as illustrated in Figures 01-05-04-01A and 01-05-04-01B. Figure 01-05-04-01A consists of a glass bulb from which air has been removed using a vacuum pump, and the neck of which is subsequently sealed by heating and drawing to a tip. Figure 01-05-04-01B shows an evacuated 3-liter sampling bomb with valve inlet and styrofoam protector. Both types of sample containers above are suitable for trapping carbon dioxide, methane and other nonreactive gases. For the sampling of H_2S, SO_2 or NO_x an in-line silica gel adsorption tube must be used in order to trap the reactive acid gases as well as particulate, as illustrated in Figure 01-05-04-01B. To fill the pre-evacuated sample containers, the sealed neck of the container or the container valve must be opened to admit the surrounding atmosphere. Figure 01-05-04-01C shows a grab purge apparatus for the collection of sample by gas displacement. The glass vessel is connected to an aspirator or hand pump at inlet B. A sample container similar to the glass bomb in construction (e.g., having inlet and exit valves) can be connected to inlet B between the glass vessel and aspirator. The glass vessel is then purged with 10-15 volumes of gas by aspiration prior to collection of the sample in order to avoid sample contamination by the original contents. The in-line container acts as a trap for any air leaks in the aspirator.		
4. APPLICATION Environmental assessment.		
A) OPERATIONAL SCOPE Method can be used on gaseous process streams, product gas, and ambient air samples for sampling inorganic gases and organics (CO_2, O_2, CH_4, CO, H_2, N_2, C_3H_8, etc.) and gases containing sulfur compounds, nitrogen oxides, etc., when suitable adsorption tubes are included in the sampling train. B) INTERFERENCES/LIMITATIONS Acid gases (H_2S, SO_2, nitrogen oxides) and particulates interfere, but may be removed by silica gel adsorption tubes positioned at the inlet end of the sample container (See Figure 01-05-04-01B and C). C) RECOMMENDED USE AREA This is applicable to the environmental assessment of fugitive gas emissions.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY 10% or better C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Sealing wax.	Sample containers, gas pumps (aspirators, hand pumps, siphons), gas metering devices, adsorption tubes.	
8. KEYWORD INDEX: Gas grab sampling, gas displacement, fugitive emissions.		
9. CROSS REFERENCE ID NUMBERS 01-01-04-01, 01-01-04-02; 02-02; 02-03; 02-01-01-07.		
10. REFERENCES		
A) PRIMARY SOURCE 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1605-60, "Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 349-370. 058 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Process Measurements, Lurgi Coal Gasification Process," TRW Systems Group, EPA Contract No. 68-02-1412, March 1975, Chapter V. B) BACKGROUND INFORMATION 052 Leithe, W., "The Analysis of Air Pollutants," Ann-Arbor Humphrey Science Publishers, Ann Arbor, Michigan, 1970. C) FIELD APPLICATIONS		

TITLE GENERAL FUGITIVE GAS GRAB SAMPLING TECHNIQUES (CONTINUED)

ID NO. 01-05-04-01

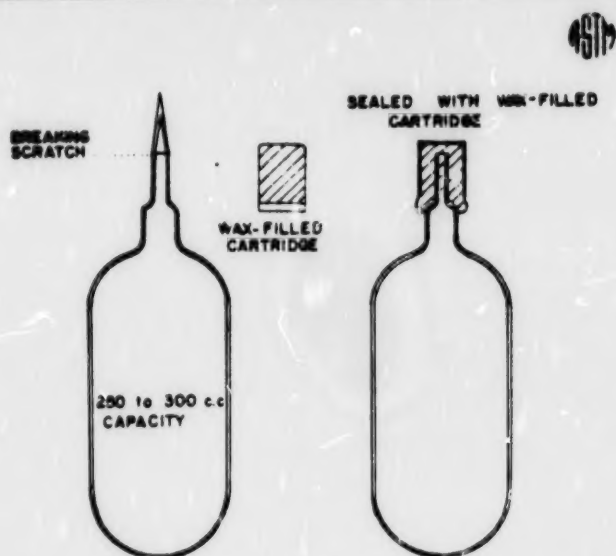


Figure 01-05-04-01A. Evacuated Sample Container.

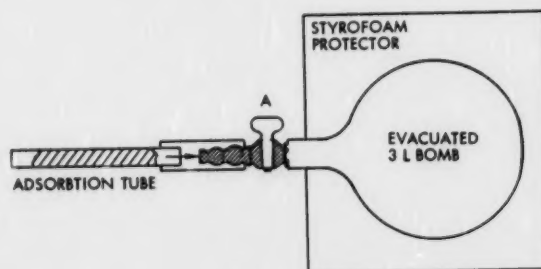


Figure 01-05-04-01B. Evacuated Grab Sampling Apparatus (3 liters).

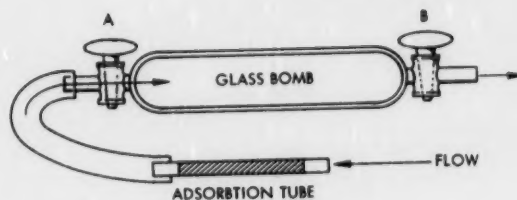


Figure 01-05-04-01C. Grab Purge Sampling Apparatus (500 ml).

1. TITLE FUGITIVE GAS GRAB SAMPLING USING PLASTIC BAGS		2. IDENTIFICATION CODE 01-05-04-02
3. ABSTRACT OF METHODOLOGY		
Plastic bags of various compositions are suitable for the collection of gas samples. Some storage properties of gases in plastic bags are shown in Table 01-05-04-02A. Figure 01-05-04-02A shows a typical integrated air sampling apparatus using a plastic sampling bag. The bag can be evacuated prior to arrival at the test site. The rigid box which houses the sample bag must be airtight and must have two openings - one for the sample inlet and the other for the pump tube. Alternatively, the bag can be filled by use of a small electric blower, or if wind velocity is sufficient, by simply pointing the bag in the direction of the wind.		
4. APPLICATION: Environmental assessment		
A) OPERATIONAL SCOPE The method is applicable to sampling of product gas, process streams, ambient air, etc. (See Table 01-05-04-02A) Plastic bags have temperature stability of several hundred degrees Celsius. B) INTERFERENCES/LIMITATIONS Method cannot be used for sulfur gases, or organics which may chemically interact. The rate of loss or contamination of sample from plastic bags, (not including direct leakage) is dependent upon type of plastic used, adsorption/diffusion characteristics for the plastic used, type and concentration of sample, temperature, pressure, and likelihood of intrasample interactions. C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment method for fugitive gas grab sampling using plastic bags.		
5. OPERATIONAL PARAMETERS		
A) RANGE Collected gases may be contained for periods of several days, with 90% or better retention. Up to several cubic feet can be collected. B) ACCURACY 10% or better. C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
See Table 01-05-04-02A for plastic bag compositions.		Plastic box for housing the bag; flowmeter, valve; pump (see Figure 01-05-04-02A).
8. KEYWORD INDEX: Fugitive gas grab sampling, plastic bags, Tedlar, Mylar.		
9. CROSS REFERENCE ID NUMBERS 01-01-04-02; 02-02-01; 02-03-01; 02-02-02; 02-03-02		
10. REFERENCES		
A) PRIMARY SOURCE 026 American Conference of Governmental Industrial Hygienists, "Air Sampling Instruments for Evaluation of Atmospheric Contaminants," Cincinnati, American Conference of Industrial Hygienists, 4th ed., 1972, p. R-5 to R-7. 024 ASTM Committee D-17 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, D1605-60, Part 23, "Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 351-2. B) INTERFERENCES/LIMITATIONS 115 Schuette, F.J., "Plastic Bags for Collection of Gas Samples," A.I.H.L. Report No. 19, California Dept. of Public Health, December 1965. 116 Smith, B.S., and J.O. Prince, "The Use of Plastic Bags for Industrial Air Sampling," <u>Amer. Indust. Hyg. Assoc. J.</u>, <u>31</u>, 343-348. 117 Altshuler, A.P., I.R. Cohen, S.F. Selva and A.F. Wartburg, "Storage of Vapors and Gases in Plastic Bags," <u>Int. J. Air Wat. Poll.</u>, <u>6</u>, 75-81 (1962). 118 Conner, W.D., and J.S. Nader, "Air Sampling with Plastic Bags," <u>Amer. Indust. Hyg. Assoc. J.</u>, <u>25</u>, 291-297 (1964).		

TITLE FUGITIVE GAS GRAB SAMPLING USING PLASTIC BAGS (CONTINUED)

ID NO. 01-05-04-02

B) BACKGROUND INFORMATION (Continued)

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- 120 Tamplin, B., Unpublished data, Air and Industrial Hygiene Laboratory, California State Department of Public Health (1963).
- 121 Schuette, F.J., Unpublished data, Air and Industrial Hygiene Laboratory, California State Department of Public Health (1962).
- 122 Ringold, A., R. Finn, J.R. Goldsmith, H.L. Helwig and F. Schuette, "Estimating Recent Carbon Monoxide Exposures," *Arch. Environ. Health*, **5**, 30-48 (1962).
- 058 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Process Measurements, Lurgi Coal Gasification Processes," EPA Contract No. 68-02-1412, TRW Systems Group, March 1975, p. 5-6.

C) FIELD APPLICATIONS

- 123 "Tentative Method for Analysis of C₁ Through C₅ Atmospheric Hydrocarbons," Review Draft (1965) Method SOPH: 1-50, Air and Industrial Hygiene Laboratory, California State Department of Public Health.
- 124 Stewart, R.D., D.S. Erley, H.H. Gay, C.L. Hake and J.E. Peterson, "Observations on the Concentrations of Trichloroethylene in Blood and Expired Air Following Exposure of Human," *Amer. Indust. Hyg. Assoc. J.*, **23**, 167-170 (1962).
- 125 O'Keefe, A.E., Private Communications, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, U.S. Public Health Service, Cincinnati, Ohio, 1965.
- 126 Wilson, K.W., and H. Buchberg, "Evaluation of Materials for Controlled Air Reaction Chambers," *Indust. Eng. Chem.*, **50**, 1705-1708 (1958).

Table 01-05-04-02A. Some Storage Properties of Vapors and Gases in Plastic Bags (Reference 115).

Plastic Film	Ref.	Gas or Vapor Stored	Concentration	Remarks
Mylar	117, 118	Ozone	70 ppms	10% loss in 5 hrs in synthetic air
	117, 118	NO ₂	0.2 to 0.5 ppm	5% in 8 hrs in synthetic air
	117, 118	SO ₂	0.5 ppm	Stable for 4 hrs in synthetic air
Polyvinyl	122	Carbon monoxide	1 to 100 ppm	Storage variable with source of supply
Scotch Pak	120	Carbon monoxide	1 to 100 ppm	Stable several days in expired air
Kel-F	126	NO ₂	1 ppm	Stable for 120 hrs

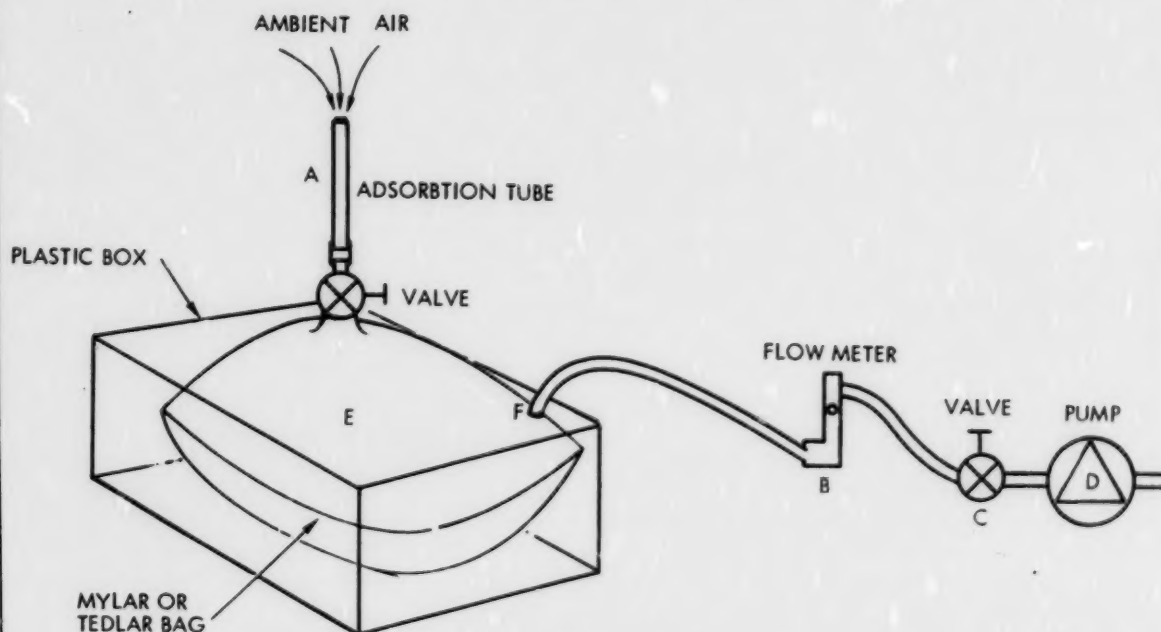


Figure 01-05-04-02A. Integrated Air Sampling Apparatus Schematic.

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01-06-01-07 Sampling Fugitive Emissions With Sequential Tape Samplers

01-06-02 Particle Sizing Techniques

01-06-02-01 Particle Sizing of Fugitive Emissions

APPLICATION MATRIX FOR 01-06 FUGITIVE PARTICULATE EMISSIONS

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
01-06-01-01			●
01-06-01-02			●
01-06-01-03			●
01-06-01-04	●	●	
01-06-01-05	●		
01-06-01-06			●
01-06-01-07			●
01-06-02-01	●		

SAMPLING FOR FUGITIVE PARTICULATE EMISSIONS - ID No. 01-06

Particulates can be chemical elements or compounds in either solid or condensed liquid droplet form. Solid particulates can be grouped into several categories, based on particle size and method of evolution. Dusts, which can range in size from visible to μm diameter particles, are formed from solids by mechanical processes such as grinding, crushing, and pulverizing. Fumes, which range in size from 1 to 0.0001 μ , are formed from solids by evaporation, condensation, and various gas phase molecular reactions. The third type of particulate matter, smokes, are products of incomplete combustion of organic materials and are characterized by optical density; the size of smoke particles is approximately 0.5 μ . If vents are sampled, then the conditions for isokinetic sampling (01-04) must be met. Ambient or enclosed areas do not need to follow those rules.

Principal process areas which are sampled for fugitive particulate emissions include coal pile storage areas, including grinding and sifting areas, gasifier input areas (lock-hoppers) and miscellaneous process vents. The general rule for particulate collection requires that enough sample be pulled through the sampler to establish a net particulate weight of 50 to 250 mg. Air flow through the filter can be adjusted so that the sample weight falls within this range over a 24-hour period. The graphs shown in Figure 01-06-A can be used as aids in obtaining the proper flow rate.

For details on the placement of sampling units and the problems collecting fugitive emissions, the reader is directed to 01-05.

01-06-01 Mass Loading Techniques (Abstracts 01-06-01-01 through 01-06-01-08)

Sampling fugitive particulate emissions requires either high flow rates or high analysis sensitivity to overcome the low mass loading normally encountered. The standard piece of equipment for particulate sampling is the high volume sampler (01-06-01-05). Because of changes in the pressure drop across the filter, it is recommended that the commercial equipment selected have an automatic constant flow rate control to insure accurate flow rate measurement. An electrostatic precipitator (01-06-01-06) is another high volume sampler. An ESP has

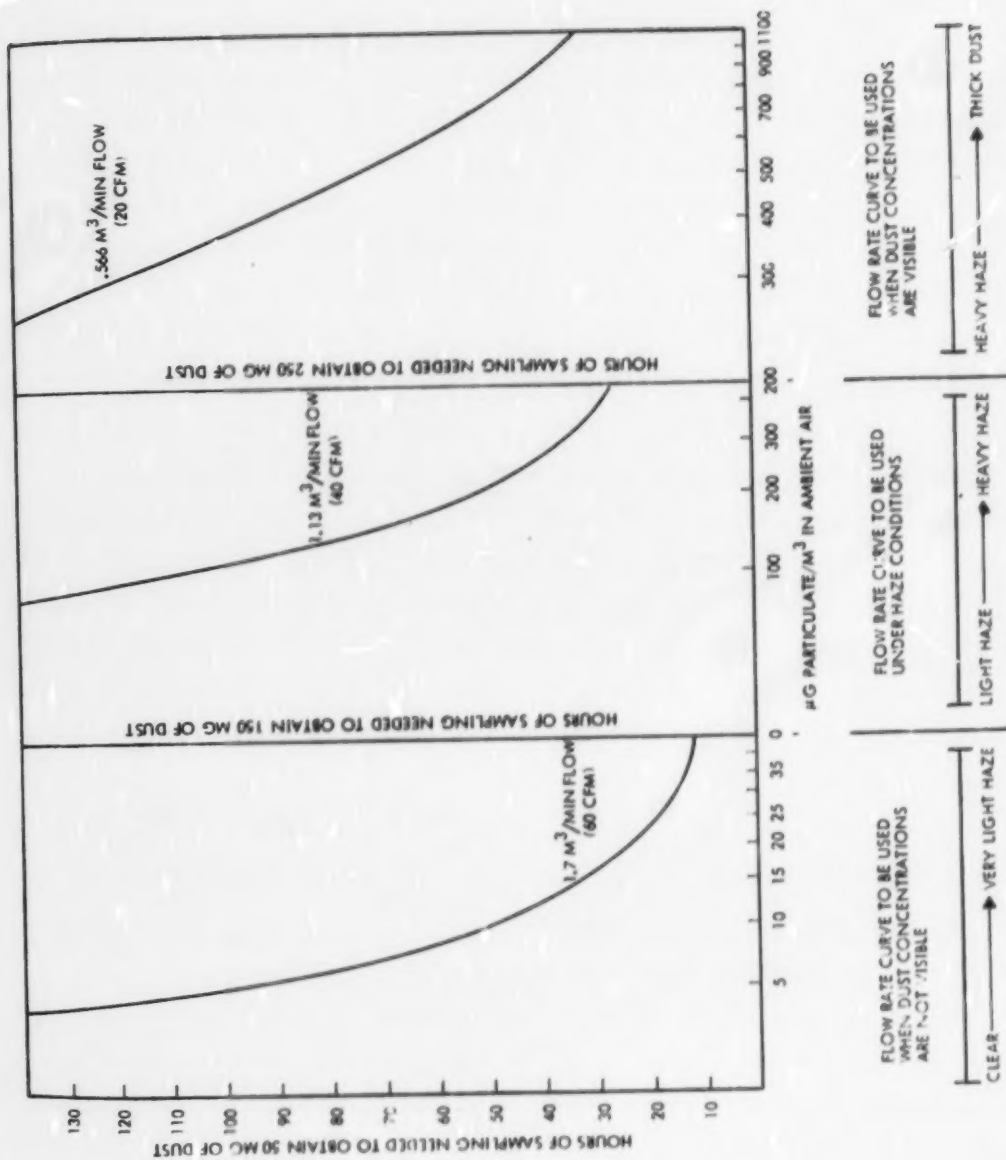


Figure 01-06-A. Sampler Flow Rate Settings for Dust (References 024 and 127)

the dual advantages of a low pressure drop and particulate collection in a small area. If semi-continuous or sequential sampling of the fugitive emissions is desired, tape samplers (01-06-01-08) can be used. Because of their lower flow rate, sampling times and analytical methods (02-01-04-04 and 02-02-01-05) must be selected carefully. An integrated sampling and analysis approach is described in 01-05-01-07 where a spectrographic graphite electrode is used to sample the air, and then analyzed by Optical Emission Spectroscopy (02-02-02-03). If mass loading information only is required, then a piezo-electric (01-06-01-03) or β attenuation (01-06-01-04) monitor can perform this task in a continuous manner. Many of the commercial instruments using these approaches collect the particulate sample for later chemical analysis. Finally, settleable particulates (01-06-01-01) are measured with standard techniques.

01-06-02 Particle Sizing Techniques (Abstract 01-06-02-01)

Analysis of fugitive emission for particle size distribution is becoming increasingly important. Concern about the distribution of the respirable portion (1-10 μ) of particulate has dictated an increase in the use of cascade impactors (01-06-02-01). Commercially available units have reasonably high flow rates (20-40 cfm) and large collection capacities.

REFERENCES

- 024 "Planning the Sampling of the Atmosphere", ASTM 1974 Annual Book of Standards, Part 23, D1357-57.
- 127 Danielson, J.A., "Air Pollution Engineering Manual", Air Pollution Control District County of Los Angeles, 2nd ed., May 1973.

1. TITLE COLLECTION AND ANALYSIS OF DUST FALL (SETTLABLE PARTICULATES)		2. IDENTIFICATION CODE 01-06-01-01
3. ABSTRACT OF METHODOLOGY		
Open-top collectors of specific size and shape are located at carefully positioned sites outdoors to collect settleable particulates. The collected material can be taken to the laboratory in a closed container for further analysis. Settleable particulates for this method are described as any particle, liquid, or solid small enough to pass through a 1 millimeter screen and large enough to settle in the collector.		
4. APPLICATION: Engineering evaluation; R&D.		
A) OPERATIONAL SCOPE This method covers the procedure for the field collection of settleable particulates, and can be used in areas where windblown dust from the ground or storage areas is not a problem. B) INTERFERENCES/LIMITATIONS Care must be taken to avoid matter from trees, bird droppings and other such deposits. Also, material collected by action of wind must be prevented. Care must be taken in selecting the sampling site to prevent undue influence from a particular source, thus biasing the composition of the particulates collected. C) RECOMMENDED USE AREA Engineering evaluation R&D fugitive emissions survey technique.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY N/Q; care must be taken in using this method because of its simple and unsophisticated approach to collection. C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Reagent grade water; isopropyl alcohol, reagent grade.		Collector (an open-top cylinder with vertical sides, flat bottom), No. 18 sieve.
8. KEYWORD INDEX: Sampling, mass loading techniques, settleable particulates.		
9. CROSS REFERENCE ID NUMBERS 01-06-01-04, 05, 07.		
10. REFERENCES		
A) PRIMARY SOURCE 013 ASTM, "Standard Method for Collection and Analysis Thus Far," 1974 Annual Book of ASTM Standards, Method D1739-70, Part 26, p. 340. B) BACKGROUND INFORMATION 128 Meethan, A.R., "Atmospheric Pollution; Its Origin and Prevention," Pergamon Press, London, 3rd ed., 1964, Chapter 11, "Measurements of Air Pollution." 129 Air Pollution Control System Association, "Recommended Standard Method for Continuous Dust Fall Survey (APH-1, Revision 1)," <u>J.A.P.C.A.</u>, 16, 372 (1966). C) FIELD APPLICATIONS 130 Nader, J.S., "Dust Retention Efficiencies of Dust Fall Collectors," <u>J.A.P.C.A.</u>, 8, 35 (1958).		

1. TITLE CONTINUOUS MONITORING OF MASS LOADINGS USING BETA ATTENUATION		2. IDENTIFICATION CODE 01-06-01-02
3. ABSTRACT OF METHODOLOGY		
Beta attenuation instruments consist of a beta radiation source (usually ^{14}C), a detector, and a tape sampler. Particles from a known volume of air are collected on a filter tape and then placed between the radiation source and detector. The difference in the detector count before and after the particles are collected is a measure of the mass of the particles.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE These units are designed for semicontinuous analysis to atmosphere. By using sampling lines and a switching system, a series of sampling points can be monitored. These systems provide a continuous measure of mass loading while at the same time collecting a sample for chemical analysis. B) INTERFERENCES/LIMITATIONS One must always be aware of the collection efficiency of the filter tape. In many cases, Whatman filter paper is used in the tape sampler; this filter ranges from 50 to 80% as efficient as glass fiber filters for smaller particles. C) RECOMMENDED USE AREA This method is used for engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE The units are completely automated and the amount of sample taken can be adjusted to compensate for high and low mass loadings. B) ACCURACY $\pm 15\%$ C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
None		A typical automatic beta continuous attenuation sampling device can be obtained from the Research Appliance Co., Allison Park, Penn. A high volume unit can be obtained from the GCA Technology Division, Bedford, Mass.
8. KEYWORD INDEX: Sampling, beta continuous.		
9. CROSS REFERENCE ID NUMBERS 02-01-02-04.		
10. REFERENCES		
A) PRIMARY SOURCE 131 Nader, J.S., and D.R. Allen, "A Mass Loading and Radioactivity Analyzer for Atmospheric Particulates," <u>Am. Indust. Hyg. Assoc. J.</u>, <u>1</u>, 300 (1960). B) BACKGROUND INFORMATION 132 Lilienfeld, P., and J. Dulchinos, "Vehicle Particulate Exhaust Mass Monitor," Final Report for EPA on Contract No. 68-02-0209 (1972). 134 Dresia, H., and F. Spohr, "Experience with the Radiometric Dust Measuring Unit," <u>Staub-Reinhalt Luft</u> (English translation), <u>31</u>, 6 (1971). C) FIELD APPLICATIONS 135 Duke, C.R., and Y.C. Boong, "Development of a Nucleonic Particulate Emission Gauge," Industrial Nucleonic Corp., Columbus, Ohio, NTIS, DB 209954, 1972. 136 Hering, R., "Beta Gauge and Filter Collection System for Determination of Automobile Particulate Emissions," preprint, Joint Conference on Sensing of Environmental Pollution, Palo Alto, Ca., Nov. 8, 1971.		

TITLE CONTINUOUS MONITORING OF MASS LOADINGS USING BETA
ATTENUATION (CONTINUED)

ID NO. 01-06-01-02

10. REFERENCES (Continued)

- 137 Huser, R.B., and S.C. Heiseler, "Proceedings from the Conference on Methods in Air Pollution Industrial Hygiene Study,"
State of California Dept. of Public Health, Berkeley, California, October 1972.

1. TITLE PIEZO-ELECTRIC AEROSOL MASS CONCENTRATION MONITOR	2. IDENTIFICATION CODE 01-06-01-03
3. ABSTRACT OF METHODOLOGY This instrument continuously monitors the aerosol mass concentration by monitoring the change in the residence frequency of a piezo-electric quartz crystal accompanying the precipitation of the particulate on the face of the crystal. Aerosol is run through the system by a vacuum pump at 1 lpm. The sampling crystal is the collecting surface of an electrostatic precipitator, which collects particles from 0.01 through 10 microns in diameter. A second crystal, not exposed to the aerosol, balances out frequency changes due to temperature, pressure and humidity changes. Recent advances have used several crystals stacked in a cascade impaction device to monitor the mass loading versus particle size on a continuous basis. The rate of change of the output frequency is directly proportional to the mass concentration of the airborne particles. Thus, mass concentration equals the change in frequency during a given time period divided by a sensitivity constant. The sensitivity constant is supplied with each unit. Direct monitoring of the output is easily accomplished by means of an electronic counter.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE This instrument has sufficient sensitivity to measure ambient particulate mass concentration and has also been used to measure particulate concentrations in flue gas (see Ref. 141 in Field Applications).	
B) INTERFERENCES/LIMITATIONS Since the piezo-electric device depends upon efficient sampling of the electrostatic precipitator, the same problems that occur with electrostatic precipitators (changes in efficiency with particle size and humidity) will affect the ultimate efficiency of the piezo-electric mass concentration monitor.	
C) RECOMMENDED USE AREA This method can be used for ambient engineering evaluation R&D.	
5. OPERATIONAL PARAMETERS	
A) RANGE A determination of particle mass concentration in the range of 100 $\mu\text{g}/\text{m}^3$ is possible.	
B) ACCURACY $\pm 10\%$ with a sampling time of 1 minute.	
C) PRECISION N/Q	
6. REAGENTS REQUIRED None	7. EQUIPMENT REQUIRED Piezo-electric Aerosol Mass Concentration Monitor (a typical piezo-electric aerosol mass concentration monitor can be obtained from Thermal Systems, Inc., St. Paul, Minn.).
8. KEYWORD INDEX: Sampling, mass loading, Piezo-electric sampler.	
9. CROSS REFERENCE ID NUMBERS 01-06-01-02.	
10. REFERENCES	
A) PRIMARY SOURCE 138 Branchley, L.D., C.D. Turley and R.G. Yaime, "Industrial Source Sampling," Ann Arbor Science Publishers, Ann Arbor, Mich., 1973.	
B) BACKGROUND INFORMATION 139 Olin, J.G., <u>Adv. Instr.</u> , 26 , 1 (1971). 140 Olin, J.G., L. Christeson and G.J. Sem, <u>Am. Ind. Hyg. Assoc. J.</u> , 32 , 209 (1971).	
C) FIELD APPLICATIONS 141 Chuan, R.L., "Application of an Oscillating Quartz Crystal to Measure the Mass of Suspended Particulate Matter," Chapter 9 in "Anal. Methods Applied to Air Pollution Measurement," edited by R.K. Stevens and W.F. Herget, Ann Arbor Science, Ann Arbor, Mich., 1974. 142 Carpenter, T.E., and L.D. Branchley, <u>Am. Ind. Hyg. Assoc. J.</u> , 33 , 503 (1972).	

1. TITLE SAMPLING FUGITIVE EMISSIONS BY HIGH VOLUME SAMPLERS		2. IDENTIFICATION CODE 01-06-01-04
3. ABSTRACT OF METHODOLOGY		
A measured and representative sample of the atmosphere under investigation is drawn through a filter media which has been specifically selected to collect the suspended particulate. Because of the low grain loadings normally found in ambient atmospheres, high volume ($3 \text{ m}^3/\text{min}$) samplers are employed. These compact and portable collectors consist of a large area filter holder, a high capacity blower, and a built-in flow indicator. In order to measure the mass concentration, a pre-conditioned (constant weight) tared filter is used to collect the sample. After the sample has been collected, the filter is then reconditioned in the same manner and reweighed. It is recommended that a Gelman Type A Spectrograde glass fiber filter be used to collect a particulate sample if chemical analysis is to be performed. As a second choice, acid-washed Whatman 41 can be used to collect the sample. If chemical analysis is to be conducted on the filter, care must be taken to avoid contamination by dust or handling methods, and at all times the filter should be transported in a container which has been suitably cleaned for trace analysis work (see 02-01-01, 03, -04).		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE This procedure covers the collection of particulate matter from an atmosphere by filtration and for the measurement of either mass loading or chemical analysis of the particulates collected. Although especially applicable to collection of solid particles, the filter method may be also used to collect liquid particles if droplet size need not be determined. B) INTERFERENCES/LIMITATIONS Large samples must be taken over a period of time and, consequently, the daily fluctuations in particle concentrations cannot be determined (for semi-continuous methods, see 01-06-01-02, -03). During the sampling period, the filter will tend to become loaded and the flow rate will decrease as filter resistance increases. Therefore, it may be necessary to adjust the flow rate frequently or provide for essentially constant flow automatically by means of a critical orifice. C) RECOMMENDED USE AREA Environmental assessment.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY The accuracy of the method will depend upon how accurately the filter is weighed and how accurately the flow rate is measured. C) PRECISION N/A		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
None	Analytical balance, desiccator, petri dishes, high volume sampling unit (typical suppliers are: Gelman Instrument Co., Chelsea, Mich.; Mine Safety Appliances, Pittsburgh, Penn.; Staplex Co., Brooklyn, N.Y.; Union Industrial Equipment, Portchester, N.Y.; Production Equipment Co., Detroit Mich.).	
8. KEYWORD INDEX: 02-01-01, 03, 04; 01-06-01-02, and 03.		
9. CROSS REFERENCE ID NUMBERS		
10. REFERENCES		
A) PRIMARY SOURCE 053 ASTM, "Collection by Filtration and Determination of Mass, Number and Optical Sizing of Atmosphere Particulates," 1974 Annual Book of ASTM Standards, Part 26, Method D2009-65, p. 422. B) BACKGROUND INFORMATION 480 U.S. Environmental Protection Agency, Title 40, Part 50, Chapter 1, Appendix B, Washington, D.C. 143 Smith, Walter J., and N.F. Surprenat, "Properties of Various Filter Media for Atmospheric Dust Sampling," <i>Proceedings, ASTM</i>, 55, 1955. 144 Silverman, L., and F.J. Biles, "A High Volume Air Sampling Filter Weighing Method for Certain Aerosols," <i>J. of Ind. Hyg. Tox.</i>, 30(2), 124. C) FIELD APPLICATIONS 145 Silverman, L., and C.R. Williams, "An Apparatus for Sampling of Large Air Volumes for Industrial Air Analysis," <i>J. of Ind. Hyg. Tox.</i>, 28, 21 (1946). 146 Katz, M., and G.D. Clayton, "Instrumentation and Analytical Techniques for the Continuous Determination of Air Contaminants," <i>Proceedings, ASTM</i>, 53, 1136 (1953). 147 Dams, R.H., and R. Heindryckx, <i>Atm. Environ.</i>, 7(3), 319 (1973).		

TITLE SAMPLING FUGITIVE EMISSIONS BY HIGH VOLUME SAMPLERS (CONTINUED)

ID NO. 01-06-01-04

C) FIELD APPLICATIONS

- 148 Pluss, T.H., and W. Strauss, Atm. Environ., 7(6), 657 (1973).
- 149 Rahn, K.A., G. Beke and G. Windels, Atm. Environ., 8, 635 (1974).
- 150 "Calibrative Study of Reference Method for Determination of Suspended Particulates in the Atmosphere," Quality Assurance and Environmental Laboratory, Environmental Protection Agency, Research Triangle, N.C., PB 205-891, June 1971.

1. TITLE FUGITIVE EMISSIONS SAMPLING WITH AN ELECTROSTATIC PRECIPITATOR	2. IDENTIFICATION CODE 01-06-01-06
3. ABSTRACT OF METHODOLOGY In the electrostatic precipitator (ESP), dust-laden air is passed between two surfaces carrying a high electric potential. This high electric potential causes the ionization of air molecules. These charged molecules can interact with the particles in the gas stream and cause them to attain a charge. Under the force of the electric field, the charged particles are then driven to a collecting electrode where they are precipitated. Normally, the collection plate is small and hence the collected particles can be weighed accurately. The precipitation is highly efficient, air flows are high, and pressure drops are low. In general, electrostatic precipitators have two important advantages over filters: 1) the sampling rate is not affected by the amount of sample collected, and 2) the sample is usually in a readily recoverable form.	
4. APPLICATION: Environmental assessment.	
A) OPERATIONAL SCOPE This method can be used to sample fugitive emissions under ambient conditions.	
B) INTERFERENCES/LIMITATIONS Electrostatic precipitators are higher in initial cost than other high volume sampling units. Because of the electrical discharge in the sampling area, they cannot be used in explosive atmospheres. This electric field also generates small amounts of ozone and oxides of nitrogen. Some units employ a positive corona discharge which lowers the amount of ozone produced. One must realize that gases such as SO ₂ passing through the corona can be oxidized to sulfuric acid and coat the particles. Subsequent chemical analysis will be jeopardized, especially if surface techniques such as ESCA are employed. Under most conditions, however, the oxidation of SO ₂ should be minimal.	
C) RECOMMENDED USE AREA This device can be used as an alternate fugitive emission sampling system.	
5. OPERATIONAL PARAMETERS	
A) RANGE Typical flowrates are from 500 to 10,000 lpm.	
B) ACCURACY At 5000 lpm, a typical unit collected 90% of 0.1u particles.	
C) PRECISION N/Q	
6. REAGENTS REQUIRED None	7. EQUIPMENT REQUIRED Typical ESP samplers can be obtained from Environmental Research Corp., St. Paul, Minn., and Del Electronic Corp., Mt. Vernon, N.Y.
8. KEYWORD INDEX: Sampling, electrostatic precipitator, ESP.	
9. CROSS REFERENCE ID NUMBERS 02-04-01, 02-04-02.	
10. REFERENCES	
A) PRIMARY SOURCE 026 "Air Sampling Instruments," American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1972.	
B) BACKGROUND INFORMATION	
151 Lipmann, M., S. Cravaugh, H.J. DiGiovanni and P. Lilienfeld, "Lightweight High Volume Electrostatic Precipitator Survey Sampler," <i>AIHA Journal</i> , 26, 485 (Sept.-Oct. 1965).	
152 Lowe, H.T., and V.H. Lucas, "The Physics of Electrostatic Precipitation," <i>Brit. J. Appl. Phys.</i> , 24, Sup. 2, 40 (1953).	
153 Liu, B.Y.H., K.T. Whitby and H.H.S. Yu, "Electrostatic Aerosol Sampler for Light and Electron Microscopy," <i>Rev. Sci. Instr.</i> , 38, 100 (1967).	
C) FIELD APPLICATIONS	

1. TITLE COMBINED SAMPLING ANALYSIS METHOD FOR DETERMINATION OF TRACE ELEMENTS ATMOSPHERIC PARTICULATES (GRAPHITE CUP)	2. IDENTIFICATION CODE 01-06-01-06
3. ABSTRACT OF METHODOLOGY	
Porous cup spectrographic graphite electrodes are used as filters to collect atmospheric particulates and then are analyzed for elements directly by an emission spectrographic method. Each graphite collection filter is solution-doped with 0.25 micrograms of indium as an internal standard and dried in a vacuum oven at atmospheric pressure prior to field use. Using the sampling device shown in Figure 01-06-01-06A, a sample is taken using a flowmeter and vacuum pump. The spectrographic analysis is carried out using a Jarrell-Ash Custom Varisource (Model 40-750). Concentrations are determined from analytical curves developed by means of appropriate standard solutions.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE This method is designed to be used for sampling atmospheric particulates. Because of its high sensitivity, it is extremely useful in sampling atmospheres using a short sampling time. B) INTERFERENCES/LIMITATIONS While the equipment in this particular technique is readily available, the techniques employed are not applicable to most laboratories. C) RECOMMENDED USE AREA This method is applicable to engineering evaluation R&D programs for ambient measurements.	
5. OPERATIONAL PARAMETERS	
A) RANGE Several elements, such as lead, which are distributed in the atmosphere as particulates at concentrations less than 0.1 $\mu\text{g}/\text{m}^3$ per cubic meter, are determined using a 30-min. collection cycle. B) ACCURACY $\pm 10-20\%$ C) PRECISION $\pm 10-20\%$	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Spectrographic electrode (Ultra carbon, No. 202), high purity nitric acid (standard solutions that were used in this technique for calibration purposes were prepared from analytical grade reagent or spectrographic metals or metal oxides).	Jarrell-Ash Custom Varisource (Model 40-750), spectrograph (Baird-Atomic 3-meter Model 169).
8. KEYWORD INDEX: Sampling, graphite cup method.	
9. CROSS REFERENCE ID NUMBERS 02-02-02-03.	
10. REFERENCES	
A) PRIMARY SOURCE 154 Seeley, J.L., and R.K. Skogerboe, "Combined Sampling Analysis Method for the Determination of Trace Elements in Atmospheric Particulates," <i>Anal. Chem.</i>, 46, 415 (1974). B) BACKGROUND INFORMATION 155 Katz, M., "Measurement of Air Pollutants," World Health Organization, Geneva, 1969. C) FIELD APPLICATIONS 156 Woodruff, R., and J.F. Leach, <i>Anal. Chem.</i>, 34, 1323 (1972). 157 Skogerboe, R.K., A.T. Kashuba and G.H. Morrison, <i>Appl. Spectr.</i>, 23, 169 (1969). 158 Bedrosian, A.J., G.H. Morrison and R.K. Skogerboe, <i>Anal. Chem.</i>, 40, 854 (1968).	

TITLE COMBINED SAMPLING ANALYSIS METHOD FOR DETERMINATION OF TRACE ELEMENTS
ATMOSPHERIC PARTICULATES (GRAPHITE CUP) (CONTINUED)

ID NO. 01-06-01-08

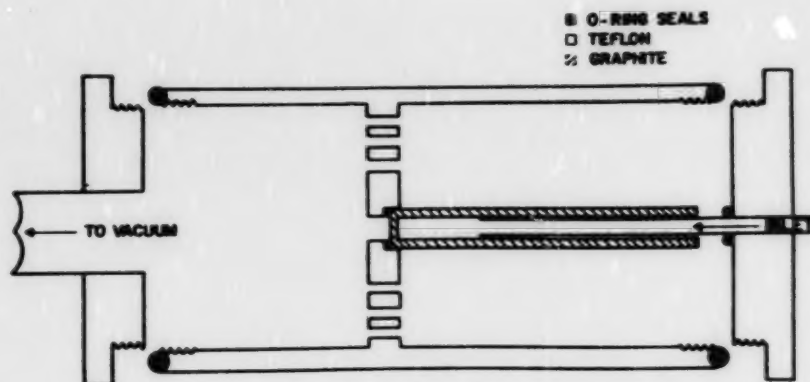


Figure 01-06-01-06A. Porous Cup Spectrographic Graphite Electrode Sampler
(from Anal. Chem., 46, 415 (1974).

1. TITLE SAMPLING FUGITIVE EMISSIONS WITH SEQUENTIAL TAPE SAMPLERS		2. IDENTIFICATION CODE 01-06-01-07
3. ABSTRACT OF METHODOLOGY		
A tape sampler uses a strip of filter paper (Whatman 41) or some related material (glass fiber) as a sampling medium. Typically this tape is about 2.54 cm (one in.) wide, 304.8 m (1000 ft.) long and is supplied in a roll form. The tape is threaded from a supply spool through an advancing mechanism and sampling head onto a take-up spool. On the sampling head the tape is supported so that an area is sealed within the sampling train. Particulates are collected by filtration (typically 10 to 20 ipm) into a narrowly defined "dust spot" on the paper. Most instruments can be automatically sequenced to intermittently advance a fresh collection surface. The individual dust spots can be returned to the laboratory for chemical analysis (see 02-01-04-04; 02-02-01-05).		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE These units are designed to sample fugitive emissions, in a sequential time-oriented mode. B) INTERFERENCES/LIMITATIONS Filtration efficiency of paper falls off with smaller particles, while the chemical blank of glass fiber is much higher than acid-washed filter paper. Under heavy dust build-up, flowrate can vary and lead to inaccuracies in mass loading calculations. C) RECOMMENDED USE AREA Collection of fugitive emission particulates for engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE Normal ambient temperatures. B) ACCURACY N/A (collection efficiency varies with particle size). C) PRECISION N/A		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
None	Tape samplers can be obtained from Gilman Instr. Co., Precision Scientific, Research Appliance Co., or National Environmental Instruments.	
8. KEYWORD INDEX: Sampling, tape sampler.		
9. CROSS REFERENCE ID NUMBERS 02-02-01-05; 02-01-04-04.		
10. REFERENCES		
A) PRIMARY SOURCE 159 "Air Quality Criteria for Particulate Matter," National Air Pollution Control Administration Publication No. AP-49, Washington, D.C., 1959. B) BACKGROUND INFORMATION 026 American Conference of Governmental Hygienists, "Air Sampling Instruments," Cincinnati, Ohio, 1972. C) FIELD APPLICATIONS 160 Chatfield, E.J., "A Battery Operated Sequential Air Concentration and Deposition Sampler," <u>Atm. Environ.</u>, 1, 509 (1967). 161 Parker, W.R., and H.A. Huey, "Multipurpose Sequential Samplers," <u>J. Air Pol. Cont. Assoc.</u>, 17, 388 (1967).		

1. TITLE PARTICLE SIZING OF FUGITIVE EMISSIONS	2. IDENTIFICATION CODE 01-05-02-01
3. ABSTRACT OF METHODOLOGY An Anderson Sampler is used to collect and size fugitive emissions. Air is drawn through the sampler, producing a jet of air from each of the 400 holes in each stage, directed at the collection plate below. The size of the holes is constant for each stage, but is smaller in each successive stage. Consequently, the jet velocity is uniform in each stage, but increases in each succeeding stage. When the velocity imparted to a particle is sufficiently great, its inertia will overcome the aerodynamic drag and the particle will impact on the surface. Thus, each stage collects smaller particles than the preceding one. Since the unit can sample up to 1 cfm of air and because of the number of the collection points, sufficient quantities of sized particulate matter can be collected for chemical or microscopic analysis. Care must be taken in site selection so that a representative sample can be obtained. (See 01-06.)	
4. APPLICATION: Environmental assessment.	
A) OPERATIONAL SCOPE This unit is designed to operate under ambient conditions to collect airborne particulate matter. B) INTERFERENCES/LIMITATIONS In many cases the collection area must be coated with a sticky material to ensure particles will not be reentrained. This procedure can interfere with chemical analysis. An additional filter is required for <0.5μ collection. C) RECOMMENDED USE AREA Particle size information for level 1 environmental assessment of fugitive emissions.	
5. OPERATIONAL PARAMETERS	
A) RANGE Ambient conditions. Six stages from 0.5 to 1μ, 1 to 2μ, 2 to 3.5μ, 3.0 to 6.0μ, 5 to 11.5μ, and >8.5μ. B) ACCURACY N/Q ($\pm 25\%$). C) PRECISION N/Q ($\pm 25\%$).	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED Anderson Sampler (Anderson 2000, Inc., Salt Lake City, Utah).
8. KEYWORD INDEX: Sampling, particle sizing.	
9. CROSS REFERENCE ID NUMBERS 02-01-03-04, (Also, appropriate chemical analyses), 01-06.	
10. REFERENCES	
A) PRIMARY SOURCE 026 "Air Sampling Instruments," <u>Am. Conf. Gov. Ind. Hyg.</u>, Cincinnati, Ohio, p. 0-23. B) BACKGROUND INFORMATION 162 Anderson, A.A., "A New Sampler for the Collection, Sizing and Enumeration of Viable Airborne Bacteria," <u>J. Bact.</u>, 76(11), 471 (1958). 163 Anderson, A.A., "A Sampler for Respiratory Health Hazard Assessment," <u>Amer. Ind. Hyg. Assoc. J.</u>, 27, 160 (March-April 1966). C) FIELD APPLICATIONS 164 Burton, R.M., et al, "Field Evaluation of the High Volume Particle Fractionating Cascade Impactor - A Technique for Respirable Sampling," presented at 65th Annual Meeting of the Air Pollution Control Association, June 1972.	

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APPLICATION MATRIX FOR 02-01 LABORATORY PREPARATION

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
02-01-01-01	●		●
02-01-01-02	●		●
02-01-01-03	●		
02-01-01-04	●	●	●
02-01-01-05	●		●
02-01-01-06			●
02-01-01-07	●		●
02-01-02-01	●		●
02-01-02-02			●
02-01-02-03	●		
02-01-03-01	●	●	●
02-01-03-02	●		
02-01-03-03	●		●
02-01-03-04	●		●
02-01-03-05	●		●
02-01-03-06			●
02-01-04-01			●
02-01-04-02			●
02-01-04-03			●
02-01-04-04			●

LABORATORY PREPARATION - ID No. 02-01

Proper sampling and analysis of inorganic samples must take into account the problems of contamination by: a) container material, b) improper cleanliness, and c) impure reagents. Standard laboratory procedures relating to cleanliness and equipment are generally acceptable for most sampling and analysis methods. However, more rigorous techniques must be used when dealing with trace level elements.

02-01-01 Reagents/Equipment Preparation (Abstracts 02-01-01-01 Through 02-01-01-07)

Sample loss and contamination due to apparatus may result if the surface of the apparatus is attacked, dissolved or etched by the sampled material. The history of the apparatus must also be considered, due to the possibility of sample contamination by previous samples which remain in the container. High temperatures, high pressures and long contact times may accelerate corrosion of the apparatus and adhesion of the sample on the container surface. Materials used in labware construction must be thermally resistant, chemically resistant, chemically inert, and also economical. Generally, the following materials are preferred: borosilicate glass, polyethylene, Teflon, platinum and fused silica. However, even these materials may contain impurities at ppm levels. Plastic labware is preferred to glassware because of its lower metal content. Table 02-01-A lists the trace elements content of some common laboratory materials compared to sea water.

Materials used in the construction of grinders, crushers, mortars and pestles, etc., must be characterized by greater hardness. Vitreous alumina, tungsten carbide and boron carbide are preferred to agate, mullite ($3 \text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and hardened steel.

Cleanliness of laboratory glassware (02-01-01-05) is a major requirement in order to prevent contamination and to avoid material losses. Chromic acid cleaning solution is widely used in cleaning of laboratory glassware; chromium usually remains on the surface of the apparatus even after rinsing. However, for trace element analysis, the use of a 1:1 concentrated sulfuric acid and concentrated nitric acid is preferred. Plastic ware can also be cleaned with mixed acids, but prolonged contact

Table 02-01-A. Trace Element Content of Sea Water and Common Laboratory Materials: PPB (165).

	Zn	Fe	Sb	Cr
Sea Water	10	10	0.3	0.5
Pyrex	730	2.8×10^5	2.9×10^3	--
Quartz	25	---	40	200
Polyethylene	25	1.1×10^4	0.8	19
Teflon	9	35	0.4	<30
Rubber	4.1×10^7	<100	360	4.2×10^5
PVC	7.1×10^3	2.7×10^5	2.7×10^3	2
Plexiglas	<10	<140	<0.01	<10
Millipore	2.4×10^3	330	39	1.8×10^4
Kimwipe	4.9×10^4	1×10^3	16	500

with the cleaning solution must be avoided in order to prevent deterioration of the polymer. After cleaning, labware must be carefully dried and stored ready for use in a manner which will preclude the possibility of inadvertent contamination.

Sample contamination by use of reagents which contain various impurities must also be avoided. Very pure reagent quality solutions (02-01-01-06) are commercially available, but these reagents may still contain ppb levels of impurities. Sample contamination may be minimized, however, by limiting the use of reagents which contain particularly undesirable contaminants.

High purity reagents (02-01-01-06) may be prepared in the laboratory when they are not commercially available, or when the purity requirements of commercial reagents are less than acceptable. A list of some common laboratory methods of high purity reagent purification and preparation are listed in 02-01-01-06. Distillations, extractions and ion exchange columns are the most commonly used methods for reagent purification. Recrystallization and zone-melting techniques may also be used.

Additional precautions which can be taken in order to minimize contamination include proper storage of reagents (02-01-01-03), the avoidance of prolonged storage of reagents, and use of minimum amounts of reagents. Reagents should be stored in clean suitable containers in clean storage spaces (drawers or cabinets). Prolonged storage of reagents must be avoided in order to prevent deterioration of reagents and to minimize risks of interaction with container walls.

The use of standards (02-01-01-02, 04) in the analysis of samples by instrumental methods is often required for accurate determinations. Since the same concentration of a species typically gives different signal strengths in different matrices, a standard is required in order to duplicate the chemical and physical nature of the sample as closely as possible. Standards must be prepared using extremely pure materials. For example, solutions of metal standards should be prepared from the pure metals using high purity acids. In order to match the matrix, special compounds in matrices are available as standards. For example, stable oil-soluble compounds are available from the National Bureau of Standards as certified standards for 24 elements in petroleum products

(02-01-01-02). Extra precautions, such as storage of the standards in desiccators, may be required in order to maximize accuracy in analysis.

Certified gas standards, such as permeation devices, dilution systems, cylinders of externally calibrated gas mixtures are commercially available and are being improved. It is recommended that the new aluminum (AIRCO) cylinders be used to store calibration gases. These containers have been shown to have $\pm 1\%$ stability over periods as long as two years (170, 171). Reliably certified zero air standards (containing 0.1 ppm maximum hydrocarbons) are currently being developed. Other standards include gaseous air pollution standards, which will permit determinations of collection efficiencies for a given particle size, range, and dust standards of known size distribution.

02-01-02 Sample Separation (Abstracts 02-01-02-01 Through 02-01-02-03)

Sample loss and contamination may arise from improper techniques (02-01-02-03) in sample separation. Sample separation may be necessary in order to isolate a specific element or species from the sample, to remove constituents which interfere with the determination, and to increase the sensitivity of the subsequent analysis by increasing the weight or volume concentration of the species of interest. Methods of sample separation include distillation (02-01-02-02), filtration (02-01-02-03), precipitation, solubilization, ion exchange (02-01-02-01), and extraction. Modern complexation methods are based on the formation of organometallic complexes, which are then separated by precipitation or solvent extractions. The major source of error in chelation and other techniques stems from incomplete separation. Other minor sources of error, which may arise from the use of impure reagents or partial decomposition of reagents due to prolonged storage, can and must be avoided.

02-01-03 Sample Handling/Preservation (Abstracts 02-01-03-01 Through 02-01-03-06)

Sample handling and preservation procedures are designed to prevent sample loss prior to analysis. Specific preservation techniques are employed for each species to be determined (02-01-03-01). In general, samples must be received, stored and handled in a clean work area. Laboratory surfaces and ventilation systems should minimize airborne

contaminants. All laboratory reagents and substances which have any possibility of contaminating the sample should be removed. After samples are received and removed from their shipping boxes, they must be wiped clean, arranged in a series, and logged on a master list. Table 02-01-B shows a sample analytical log and checklist. A preliminary examination of the sample is then conducted; all particulate samples are weighed (02-01-03-04, 05, 06), all liquid volumes are measured (02-01-03-03) and the appearance of any precipitates, organic films or scums and discolorations are noted. After the preliminary sample preparation has been completed, the appropriate separation and dissolution procedures can be followed.

02-01-04 Sample Dissolution (Abstracts 02-01-04-01 Through 02-01-04-04)

Standard procedures may involve dry or wet ashing procedures (02-01-04-01, 02). Sample losses in dry ashing procedures may result from volatilization of As, B, Cd, Cr, Cu, Fe, Pb, Hg, Ni, P and V as metals, chlorides and organometallic compounds; from adsorption of trace elements on walls of vessels and foaming of the sample during heating; from incomplete sample oxidation. Wet ashing procedures, in which the sample is oxidized with liquid reagents and which generally use lower temperatures, are preferred to dry ashing procedures due to ease in sample recovery. However, there is still a danger of loss of Sb, As, B, Cr, Ge, Hg, Se, Sn, P, Os, Re, Ru and Au by volatilization. In some cases, dissolution by organic chelate extraction of solid materials is possible (02-01-04-04). However, in all wet methods, sample contamination due to the physical manipulations are disadvantages. For trace element analysis, the use of the low temperature oxygen plasma asher is recommended (02-01-04-03). This method has been shown to be most effective in minimizing loss of trace elements due to volatilization.

Other forms of sample loss or contamination, can be anticipated and avoided. Personnel working with trace elements should minimize use of cosmetics, tobacco, etc., which could disperse through the air. The paint and coatings of walls and ceilings may act as sources of contamination, since they contain Ba, Pb, Sb, Ti and Zn. Paints based on epoxy amide resins are generally recommended. At all times a thorough system of reagent and system blanks should be run to quantify and identify possible problem areas.

Sample Identification	Date Rec'd	Prelim. Wt./Vol.	Physical Examination	Sample Work Up					Analysis	
				Drying	Grinding	Blending	Oxygen Plasma Ashing	Dissolu- tion		Pre- Concen- tration
(Cross ref- erence to sample number)			I					II	III	IV

- NOTES: 1. Insert dates at completion of each increment and the analyst's initials.
2. Describe any anomalous behavior, i.e., formation of precipitates, discoloration, films, scums, effervescence, etc.
3. (N) denotes data and procedure review points.

Table 02-01-B. Sample of Analytical Test Checklist.

REFERENCES

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- 166 Morrison, G.H., "Trace Analysis; Physical Methods," Interscience Publishers, New York, 1965.
- 167 Pinta, M., "Detection and Determination of Trace Elements," Ann Arbor Science Publishers, London, 1962.
- 168 Meinke, W. Wayne, and B.F. Scribner (eds.), "Trace Characterization; Chemical and Physical," NBS Monograph 100, Washington, 1967.
- 169 McAdie, H.G., and F.J. Hapton, "The Need for Practical Standards in Air Pollution Measurement," American Laboratory, p. 13-20, December 1975.
- 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements; Trace Inorganic Materials," EPA Contract No. 68-02-1393, July 1975.
- 014 Hamersma, J.W., and S.L. Reynolds, "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," EPA Contract No. 68-02-1412, March 1975.
- 170 Grieco, H.A., and S.G. Wechter, "The Trouble with Reactive Calibration Gas Blends and What to Do About It," presented at Gulf Coast Instrumental Analysis Conference at Houston, Texas, November 1, 1974.
- 171 Wechter, S.G., "Preparation of Stable Pollution Gas Standards Using Treated Aluminum Cylinders," presented at ASTM Calibration Symposium at Boulder, Colorado, August 5, 1975.

1. TITLE REAGENT QUALITY WATER (FOR PREPARATION, CLEANING OF SAMPLE CONTAINERS)	2. IDENTIFICATION CODE 02-01-01-01
3. ABSTRACT OF METHODOLOGY Type I reagent water, which is used with trace analysis methods is prepared by distilling water having a maximum electrical conductivity of 20 micromhos/cm at 25°C (77°F) from glass or Teflon apparatus, followed by further purification with a mixed bed of ion exchange materials. Type II reagent water, which is used for general laboratory testing, is prepared by single distillation from a glass or Teflon apparatus. Reagent water must conform to specifications shown in Table 02-01-01-01A.	
4. APPLICATION: Engineering evaluation R&D, environmental assessment.	
A) OPERATIONAL SCOPE This is the recommended procedure for the preparation of all reagent quality waters. Reagent waters are suitable for use in all standard methods of chemical analyses of all collected samples, where appropriate. (See 02-02-01-01 through 02-02-01-18; 02-03-02-01 through 02-03-02-21)	
B) INTERFERENCES/LIMITATIONS The ion-exchange process used in preparing Type I water may add organic contaminants.	
C) RECOMMENDED USE AREA This is the recommended method for preparation of reagent quality water for all engineering evaluation R&D.	
5. OPERATIONAL PARAMETERS	
A) RANGE See Table 02-01-01-01 for reagent water specifications.	
B) ACCURACY N/A	
C) PRECISION N/A	
6. REAGENTS REQUIRED Potassium permanganate solution (ACS reagent grade), concentrated sulfuric acid (ACS reagent grade), Type I water.	7. EQUIPMENT REQUIRED Apparatus for determining particulate matter, including sample reservoir, evaporation apparatus (i.e., dust shield, evaporator assembly, electronic control circuit, etc.).
8. KEYWORD INDEX: Reagent water specification; water for analysis; reagent preparation; equipment cleaning.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01; 02-02-01-01 through 02-02-01-18; 02-03-02-01 through 02-03-02-21	
10. REFERENCES	
A) PRIMARY SOURCE 024 ASTM Committees D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D-1193-70, "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 196-7.	
B) BACKGROUND INFORMATION	
024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D-1888, "Standard Method of Test for Particulate and Dissolved Matter in Industrial Water," p. 448-457.	
024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D-1125, p. 156-161.	
024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, E-200, p. 868-885.	
C) FIELD APPLICATIONS	

TITLE REAGENT QUALITY WATER (FOR PREPARATION, CLEANING OF SAMPLE CONTAINERS) (CONTINUED)

ID NO. 02-01-01-01

Table 02-01-01-01A. Requirements for Type I and Type II Reagent Water (Reference 024).

Reagent water shall conform to the following requirements:		
	Type I	Type II
Total matter, max, mg/liter (ppm) ⁽¹⁾	0.1	2.0
Electrical conductivity, max, micromhos/cm at 25°C (77°F) ⁽²⁾	0.1	5.0
Consumption of potassium permanganate ⁽³⁾	pass test	pass test
⁽¹⁾ Total matter is determined in accordance with Method A of ASTM D-1888, Test for Particulates and Dissolved Matter in Industrial Water (Reference 024).		
⁽²⁾ Electrical conductivity is determined in accordance with ASTM Method D-1125, Test for Electrical Conductivity of Water (Reference No. 024).		
⁽³⁾ Consumption of potassium permanganate is determined by adding 0.20 ml of KMnO_4 solution (0.316 g/liter) to a mixture of 500 ml of reagent water and 1 ml of H_2SO_4 in a stoppered bottle of chemically resistant glass.		

1. TITLE NBS CERTIFIED STANDARDS FOR ELEMENTS IN LUBRICATING OILS	2. IDENTIFICATION CODE 02-01-01-02
3. ABSTRACT OF METHODOLOGY Table 02-01-01-02A lists stable, oil-soluble compounds which are certified standards for 11 elements commonly found in petroleum products. A solution of one or more elements can be prepared by placing 5 ml of 2-ethylhexanoic acid, 4 ml of 6-methyl-2,4-heptanedione, and 2 ml of xylene in a flask, followed by addition of the required weight of certified standard (see Table 02-01-01-02A). The solution is then heated until the salt dissolves; this procedure is repeated for each standard added. Two ml of bis (2-ethylhexyl) amine is added, followed by the addition of cool lubricating oil. The solution is reheated to 85°C, allowed to cool and stored until use.	
4. APPLICATION: Environmental assessment, engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to the identification of trace metals in organic liquids including Ba, Cd, Ca, Cr, Cu, Pb, Mn, Ni, Sr, V, and Zn.	
B) INTERFERENCES/LIMITATIONS Minimal, if proper precautions are taken in the preparation of the certified stock solutions.	
C) RECOMMENDED USE AREA These standards are applicable to all use areas as trace analysis standards for fuels.	
5. OPERATIONAL PARAMETERS	
A) RANGE N/Q	
B) ACCURACY ±10% or better relative area.	
C) PRECISION ±10% or better.	
6. REAGENTS REQUIRED See Table 02-01-01-02A.	7. EQUIPMENT REQUIRED Standard atomic absorption spectrometer.
8. KEYWORD INDEX: Trace element analysis, atomic absorption spectrometry, certified organic standards.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02; 02-02-01-05.	
10. REFERENCES	
A) PRIMARY SOURCE 014 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," TRW Systems Group, EPA Contract No. 68-02-1412, March 1975.	
B) BACKGROUND INFORMATION 172 Dean, J.A., and T.C. Rains, "Flame Emission and Atomic Absorption Spectrometry," New York, Marcel Dekker, Inc., 1971. 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Materials," TRW Systems Group, EPA Contract No. 68-02-1393, February 1975.	
C) FIELD APPLICATIONS	

TITLE NBS CERTIFIED STANDARDS FOR ELEMENTS IN LUBRICATING OILS (CONTINUED)

ID NO. 02-01-01-02

Table 02-01-01-02A. Standard Reference Materials in Lubricating Oil
(Element of Interest, 500 µg/g) (Reference 014).

NBS No. ^a	Element of Interest	Compound	Drying time, hr ^b	Weight used, g ^c
1051b	Ba	Cyclohexanebutyrate	24	0.174
1053	Cd	Cyclohexanebutyrate	48	0.202
1074a	Ca	2-Ethylhexanoate	48	0.373
1078	Cr	Tris (1-phenyl-1,3-butanediono)-chromium (III)	1	0.515
1080	Cu	Bis (1-phenyl-1,3-butanediono)-copper (II)	0.5	0.303
1059b	Pb	Cyclohexanebutyrate	48	0.136
1062a	Mn	Manganese (II) cyclohexanebutyrate	48	0.362
1065b	Ni	Cyclohexanebutyrate	48	0.360
1070a	Sr	Cyclohexanebutyrate	24	0.242
1052b	V	Bis (1-phenyl-1,3-butanediono)-oxovanadium (IV)	2	0.348
1073b	Zn	Cyclohexanebutyrate	48	0.299

^aNational Bureau of Standards (U.S.) standard reference material.^bDried over P₂O₅ in desiccator.^cWeight of dried material which contains 50 mg of element of interest.^dDried in oven at 110°C.^eWeight of element, 20 mg, and gives a final concentration of 200 µg/g.

1. TITLE STORAGE OF REAGENTS USED IN CHEMICAL ANALYSES	2. IDENTIFICATION CODE 02-01-01-03						
3. ABSTRACT OF METHODOLOGY Glass containers are suitable for the storage of most standard acidic or neutral reagent solutions; polyolefin containers (e.g., high density polyethylene, polypropylene are preferred) are recommended for the storage of alkaline solutions. (See 02-01-01-05 for suitable cleaning procedures of polyolefin containers.) When large quantities of solutions are prepared, care must be taken to avoid changes in normality due to the absorption of gases or water vapor from the ambient air. As volumes of solution are withdrawn from the original container, the incoming air should be passed through a drying tube filled with sections of 8-to 20-mesh soda lime, oxalic acid and 4-to 8-mesh anhydrous calcium chloride, with each separate section separated by a glass wool plug. Once prepared, most standard solutions (1,000 ppm) should be periodically restandardized as a precautionary measure. Dilute solutions (<1,000 ppm) should be prepared fresh from stock solutions prior to use.							
4. APPLICATION: Environmental assessment.							
A) OPERATIONAL SCOPE Method is applicable to the storage of reagent solutions for use in the recommended analytical procedures (see 02-02, 02-03) for samples obtained from all types of effluent streams. B) INTERFERENCES/LIMITATIONS See (3) above for discussion of interferences by absorption of gases or water vapor during container transfers. Hg could cause interference if not present in the ionic state. C) RECOMMENDED USE AREA This is the recommended method for storage of chemical reagents used in all the analytical procedures.							
5. OPERATIONAL PARAMETERS							
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%;">A) RANGE</td> <td>N/A</td> </tr> <tr> <td>B) ACCURACY</td> <td>N/A</td> </tr> <tr> <td>C) PRECISION</td> <td>N/A</td> </tr> </table>		A) RANGE	N/A	B) ACCURACY	N/A	C) PRECISION	N/A
A) RANGE	N/A						
B) ACCURACY	N/A						
C) PRECISION	N/A						
6. REAGENTS REQUIRED 8- to 20-mesh soda lime; oxalic acid; 4- to 8-mesh anhydrous calcium chloride for drying tube.	7. EQUIPMENT REQUIRED Glass containers of appropriate size for storage of acidic and neutral solutions; polyolefin containers (polyethylene or polypropylene) containers of appropriate size for storage of alkaline solutions; drying tube; tubing for solution transfer.						
8. KEYWORD INDEX: Reagent storage, polyolefin containers.							
9. CROSS REFERENCE ID NUMBERS See Sections 02-02 and 02-03; 02-01-01-01, 02-01-01-05.							
10. REFERENCES							
A) PRIMARY SOURCE 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, E200-67, "Preparation, Standardization and Storage of Standard Solutions for Chemical Analysis," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 870. B) BACKGROUND INFORMATION 173 ASTM Committee E-2, E-3 and E-16, "Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores," 1971 Annual Book of ASTM Standards, Part 32, "Apparatus, Reagents and Safety Precautions for Chemical Analysis of Metals," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 282-328. C) FIELD APPLICATIONS							

1. TITLE NBS STANDARD REFERENCE MATERIALS FOR COAL AND FLYASH	2. IDENTIFICATION CODE 02-01-01-04
3. ABSTRACT OF METHODOLOGY	
It is recommended that prior to an actual sampling and analysis task, all the selected analytical techniques be tested in the laboratory with NBS standards. This dry run of sample preparation, dissolution and analysis using Standard Reference Materials (SRMs) will uncover any flaws in methodology, as well as acting as a check of the accuracy of the actual analysis. For environmental inorganic samples, NBS SRM 1632 (coal) and SRM 1633 (coal fly ash) offer a rigorous test of the precision and accuracy of an environmental analysis laboratory. They also can act as a blind test of commercial laboratories that are contracted to perform selected analyses.	
4. APPLICATION: All levels.	
A) OPERATIONAL SCOPE This recommended methodology is designed to act as a check of the accuracy and precision of the personnel, equipment and laboratory involved in the chemical analysis. B) INTERFERENCES/LIMITATIONS There are a limited number of elements certified in each SRM. Other researchers have determined other elements in the samples and their results can be used as a guide for comparison (see references, background information). C) RECOMMENDED USE AREA These standards are applicable to all areas when standards for trace element analysis of fuels are required.	
5. OPERATIONAL PARAMETERS	
A) RANGE Trace element content. B) ACCURACY NBS certified. C) PRECISION NBS certified.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Reagents required will be dictated by the choice of method and preparation procedures.	Depends on analytical methods of choice.
8. KEYWORD INDEX: SRM, analysis, NBS standards.	
9. CROSS REFERENCE ID NUMBERS 02-02; 02-03; 02-04.	
10. REFERENCES	
A) PRIMARY SOURCE 174 "Catalog of NBS Standard Reference Materials," NBS Special Publication #260, U.S. Dept of Commerce, National Bureau of Standards, June 1975. B) BACKGROUND INFORMATION 175 Ondov, J.M., et al, "Elemental Concentrations in NBS Environmental Coal and Flyash Standard Reference Materials," <u>Anal. Chem.</u>, <u>47</u>, 1102 (1975). C) FIELD APPLICATIONS	

1. TITLE CLEANING PROCEDURES FOR LABORATORY GLASSWARE AND PLASTIC LABWARE	2. IDENTIFICATION CODE 02-01-01-05
3. ABSTRACT OF METHODOLOGY	
The stepwise procedure for preparation of labware for analytical use can be stated as follows: (1) Remove old labels or markings with acetone or dry abrasive cleaners (Ajax, Dutch cleanser, etc.). (2) Wash with 2:1 solution of Alconox or dry abrasive cleaner; rinse with tap water. Thoroughly rinse pipets and volumetric flasks. (3) Rinse with the appropriate acid wash. Aqua regia (3:1 HCl-HNO₃) is used on all labware used in Hg analysis. H₂SO₄-HNO₃ in a 1:1 ratio is used on all other glassware, except volumetric flasks, for which concentrated warm (60°C) sulfuric acid is used. Twenty percent nitric acid is used for plastic labware. A 24-hour soaking in chromic acid (100 g K₂Cr₂O₇ per 3.5 liter H₂SO₄) is required for pipets. (4) Rinse once with tap water; flush 3 times with high purity water (see 02-01-01-01). (5) Dry and store for use. Flasks with glass stoppers should be capped immediately after rinsing and stored. Open-mouth glassware should be turned upside down on a rack and allowed to dry in an area free from contaminating drafts. One to 5 ml high purity water should be poured into volumetric flasks, the glass stoppers inserted, and the flask inverted several times to see that the water flows smoothly and no beading occurs in the neck (all the water to remain while storing). All labware should be stored in clean, closed cabinets or drawers.	
4. APPLICATION: Engineering evaluation R&D, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to preparation of labware for analysis, including trace element analysis of liquids and slurries, impinger solutions, bulk solids, particulate, matter, etc. B) INTERFERENCES/LIMITATIONS N/A C) RECOMMENDED USE AREA These are recommended procedures for preparation of all laboratory glassware and containers for analytical use in trace analysis.	
5. OPERATIONAL PARAMETERS	
A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Alconox, dry abrasive cleaners (Ajax, Dutch cleanser, etc), acetone, concentrated acids (hydrochloric, nitric, sulfuric), potassium dichromate.	N/A
8. KEYWORD INDEX: Cleaning, labware, glassware, analysis.	
9. CROSS REFERENCE ID NUMBERS 02-01-01-01, 02-01-01-07.	
10. REFERENCES	
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedure for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975, p. 7-1 and 7-2. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1193-70 "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 196-7. C) FIELD APPLICATIONS	

1. TITLE PREPARATION OF HIGH PURITY REAGENTS FOR TRACE ANALYSIS		2. IDENTIFICATION CODE 02-01-01-06
3. ABSTRACT OF METHODOLOGY		
Laboratory methods of purification and preparation of some common reagents used for separations in trace analysis are shown in Table 02-01-01-06A. Although distillations are most widely used for volatile reagents, various other separation methods are also useful for purifying reagents. For example, heavy metal impurities are satisfactorily removed from neutral aqueous solutions of various salts by extraction with a carbon tetrachloride solution of dithizone or with a chloroform solution of oxine, and from hydrochloric acid by passing through an anion exchange resin column. Table 02-01-01-06A summarizes the recommended procedures for purification.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE These procedures are designed to remove trace impurities from laboratory reagents. B) INTERFERENCES/LIMITATIONS These methods require scrupulous cleaning of all glassware involved in the purification procedure. Because of the time and cost involved in batch purifications, commercial high purity reagents are recommended. C) RECOMMENDED USE AREA This method is useful when high purity materials are required and not commercially available.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
See Table 02-01-01-06A.	Glass/teflon distillation apparatus, laboratory glassware.	
8. KEYWORD INDEX: Analysis, high purity reagents.		
9. CROSS REFERENCE ID NUMBERS 02-01-01-03, 05.		
10. REFERENCES		
A) PRIMARY SOURCE 166 Morrison, G.H. (ed.), "Trace Analysis Physical Methods," Interscience Publishers, New York, N. Y., 1965. B) BACKGROUND INFORMATION 176 Thiers, R.E., in "Methods of Biochemical Analysis," D. Glick (ed.), Vol. 5, Interscience Publishers, New York, 1957, p. 273. 177 Irving, H., and J.J. Cox, <i>Analyst</i>, 83, 526 (1958). 178 Wickbold, R., <i>Z. Anal. Chem.</i>, 171, 81 (1959). 179 Rees, W.T., <i>Analyst</i>, 87, 202 (1962). 180 Steinemann, H., <i>Z. Anal. Chem.</i>, 154, 267 (1957). C) FIELD APPLICATIONS		

TITLE PREPARATION OF HIGH PURITY REAGENTS FOR TRACE ANALYSIS (CONTINUED)

ID NO. 02-01-01-06

Table 02-01-01-06A. (From Morrison, "Trace Analysis," Ref. 166).

Recommended Laboratory Methods of Purification and Preparation of High Purity Reagents		
Reagent	Method	Background Information Reference
Water	Ion exchange followed by distillation	176
HCl	Dissolution of anhydrous HCl gas in pure water	
HNO ₃	Repeated distillation of 65% HNO ₃	
H ₂ SO ₄	Repeated distillation	
HClO ₄	Repeated distillation	178, 179
HF	Distillation	
	Dissolution of HF gas in pure water	180
NH ₄ OH	Dissolution of anhydrous NH ₃ gas in pure water	176
NaOH	Conversion of NaCl (purified by extraction with oxine and dithizone) with an OH-form anion exchange resin	
KOH	Conversion of KCl (purified by extraction with oxine and dithizone) with an OH-form anion exchange resin	

1. TITLE GAS SAMPLING CONTAINER CLEANING PROCEDURE		2. IDENTIFICATION CODE 02-01-01-07
3. ABSTRACT OF METHODOLOGY		
Sample containers used in gas sampling procedures should be constructed of chemically resistant glass in order to avoid sample contamination. New containers should be conditioned prior to use by allowing them to stand full of distilled water for several days. Conditioning may be accelerated by treatment with dilute hydrochloric acid. Prior to use, the containers should be thoroughly cleaned in order to remove extraneous dirt. A 2:1 mix of Alconox or abrasive cleaner and water may be used on the exterior and interior of the container, followed by rinsing with tap water. The container is then rinsed with an acid wash; an aqua regia (3:1 HCl-HNO₃) acid cleaning solution is used on all labware involved in Hg analysis, while a 1:1 H₂SO₄-HNO₃ is used on all remaining glassware (see 02-01-01-05). After tap water rinsing of the acid, the sample container is immediately flushed with 3 volumes of high purity water. The container is then filled with deionized water prior to storage.		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to preparation of all glass sampling containers used in gas sampling. B) INTERFERENCES/LIMITATIONS N/A C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D and environmental assessment procedure for the preparation of glass containers for sampling gases.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Alconox or abrasive cleaner (Ajax, Dutch cleanser, etc), deionized water; aqua regia (3:1 HCl-HNO ₃), concentrated sulfuric acid, concentrated nitric acid.		N/A
8. KEYWORD INDEX: Container cleaning procedure, gas sampling.		
9. CROSS REFERENCE ID NUMBERS 02-01-01-01, 02-01-01-05, 01-05-04-01; 01-01-04-01.		
10. REFERENCES		
A) PRIMARY SOURCE 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1192, "Standard Specification for Equipment for Sampling Water and Steam," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 190-194. B) BACKGROUND INFORMATION 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975, Chapter VII. C) FIELD APPLICATIONS		

1. TITLE ION EXCHANGE METHOD FOR THE ISOLATION OF FLUORIDE FROM ENVIRONMENTAL SAMPLES		2. IDENTIFICATION CODE 02-01-02-01
3. ABSTRACT OF METHODOLOGY		
Fluoride is removed from solution by preferential absorption on an ion exchange resin followed by desorption of fluoride in a small volume of eluting solution. Concentration of fluoride from an impinger or bubbler collection medium may be achieved without danger of contamination from prolonged exposure of solutions, such as occurs with steam distillation.		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE This method is applicable to any environmental sample which requires isolation handling of small quantities of fluoride. B) INTERFERENCES/LIMITATIONS This method removes interfering cations by absorbing the fluoride on the anion exchange resin, allowing the cations to pass through. The fluoride is then eluted with sodium hydroxide solution. Aluminum or Si will interfere by forming complexes with F⁻. C) RECOMMENDED USE AREA Recommended for any sample at any level where less severe interferences to fluoride measurement exist. The Willard/Winter distillation is the recommended procedure where Al and Si are present (see 02-01-02-02).		
5. OPERATIONAL PARAMETERS		
A) RANGE Microgram to low milligram quantities. B) ACCURACY +5% Note: Low recovery indicates incomplete preconditioning of a new column, while high recovery may be due to contamination or failure to elute the previous sample. C) PRECISION N/Q (+5% estimated).		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Anion exchange resin [Duolite A-41, A-43; Ionac A302; PERMUTIT A; REXYN 205(OH)], hydrochloric acid, sodium hydroxide, quartz sand.		Chromatography column, lab glassware.
8. KEYWORD INDEX: Analysis, fluoride analysis, ion exchange, fluoride.		
9. CROSS REFERENCE ID NUMBERS 02-03-02-01, 02-03-02-02, 02-01-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 103 ASTM, "Tentative Methods for Analysis for Fluoride Content of Atmosphere and Plant Tissue (Manual Procedures)," 1974 Annual Book of ASTM Standards, Part 26, D3269-73T, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 735. B) BACKGROUND INFORMATION 181 Newman, A.C.D., "Separation of Fluoride Ions from Interfering Ions and Cations by Anion Cation Exchange Chromatography," Anal. Chim. Acta, 19, 471 (1958). C) FIELD APPLICATIONS 182 Nielson, A.P., and A.D. Dangerfield, "Use of Ion Exchange Resin for Determination of Atmospheric Fluorides," A.M.A. Archives of Industrial Health, 11, 61 (1955).		

1. TITLE WILLARD WINTER DISTILLATION FOR THE ISOLATION OF FLUORIDE FROM ATMOSPHERIC SAMPLES		2. IDENTIFICATION CODE 02-01-02-02
3. ABSTRACT OF METHODOLOGY The prepared sample is distilled from a strong acid such as sulfuric or perchloric in the presence of a source of silicate. Fluoride is steam distilled as the fluorosilicic acid under conditions permitting a minimum of volatilization and an entrainment of liberating acid. Samples relatively free of interfering materials and containing easily liberated fluoride forms can be subjected to a single dissolution from perchloric acid at a 135°C. Samples containing aluminum, boron or silicon may require a higher temperature and a larger volume of distillate for quantitative recovery. In this case, a preliminary displacement from sulfuric acid at 165°C is commonly used. Chlorides are separated by precipitation with silver perchlorate.		
4. APPLICATION: Engineering evaluation R&D		
A) OPERATIONAL SCOPE This distillation procedure can be used for any environmental sample provided that major interferences such as aluminum, silicon and boron are not present. In the event that these three are present, the double dissolution procedure is the recommended mode of operation.		
B) INTERFERENCES/LIMITATIONS Not useful for low level fluoride.		
C) RECOMMENDED USE AREA Engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE From 1 mg to 100 mg.		
B) ACCURACY In general, recoveries will be $\pm 10\%$ of the fluoride present.		
C) PRECISION Standard deviations under favorable circumstances have been as low as 0.5%.		
6. REAGENTS REQUIRED Perchloric acid, silver perchlorate and sulfuric acid.		7. EQUIPMENT REQUIRED Steam generator, distillation flask, Liebig condenser, steam release tube, thermometer, support plate, receiver, safety tube, rubber tubing, soft glass beads, boiling chips, pinch cock.
8. KEYWORD INDEX: Analysis, fluoride analysis, fluoride dissolution.		
9. CROSS REFERENCE ID NUMBERS 02-01-02-01; 02-03-02-01, 02-03-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 013 ASTM, "Tentative Methods for Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures)," 1974 Annual Book of ASTM Standards, Part 26, Method D3269-731, p. 735.		
B) BACKGROUND INFORMATION 183 Willard, H.H., and O.B. Winter, "Volumetric Method for Determination of Fluoride," <u>Ind. Eng. Chem. Anal.</u> , 5th ed., 5, 7 (1933).		
C) FIELD APPLICATIONS 184 Smith, F.A., and D.E. Gardner, "The Determination of Fluoride in Urine," <u>Am. Ind. Hyg. Assoc.</u> , 16, 215 (1955).		

1. TITLE SEPARATION OF LIQUID/SLURRY SAMPLES	2. IDENTIFICATION CODE 02-01-02-03
3. ABSTRACT OF METHODOLOGY	
Once a liquid or liquid/slurry sample is collected, it must be properly stored prior to return to the laboratory. In many cases, it is desirable to separate the filterable and nonfilterable solids from the liquid and store them in separate containers for analysis in the laboratory. Filterable (dissolved) solids are those which pass through a standard glass fiber filter; they are determined by evaporation of the filtrate to constant weight at 180°C (356°F). Nonfilterable (suspended) solids are those which are retained by a standard glass fiber filter; retained residues are then determined by drying to constant weight at 103-105°C. Total solids (suspended solids and dissolved materials) are quantitatively determined by evaporation to dryness in an evaporation dish and weighing. Figure 02-01-02-03A outlines the separation techniques required to separate water-solid, water-organic liquid, and water or organic liquid-solid streams into their component parts. Addition of nitric acid to one-half of the filtrate is designed to keep most cations in solution and to prevent them from absorbing on the polyethylene container walls. On the other hand, sodium hydroxide is added to stabilize anions such as cyanide during shipment. (For specific additives to samples for preservation see 02-01-03-01.)	
4. APPLICATION: Environmental assessment.	
A) OPERATIONAL SCOPE These methods are designed to be used on any stream containing solids, liquids, and organic liquids in any combination. B) INTERFERENCES/LIMITATIONS In general, the addition of nitric acid or sodium hydroxide should not interfere with any analytical procedures to be performed on the sample. The analyst must always remember the ultimate analysis goal of the collected samples, and prevent separations or reagent additions from interfering with his analysis scheme. C) RECOMMENDED USE AREA Preservation of samples for environmental assessment.	
5. OPERATIONAL PARAMETERS	
A) RANGE 10 to 20,000 mg/liter of dissolved solids; 20 to 20,000 mg/liter suspended solids; 10 to 30,000 mg/liter total solids; N/Q for volatile solids. B) ACCURACY N/A C) PRECISION Standard deviation of ±11 mg/liter at 170 mg/liter volatile solids concentration was determined for 4 samples in 3 laboratories.	
6. REAGENTS REQUIRED High purity nitric acid, high purity sodium hydroxide, high purity methanol, high purity distilled water.	7. EQUIPMENT REQUIRED Teflon filters, Nalgene separatory funnel, Nalgene filter flask, Nalgene vacuum pump; Gelman Spectrograde glass fiber filters (or equivalent), Nalgene Buchner funnel, laboratory oven (103-105°C, 180°C).
8. KEYWORD INDEX: Analysis, sample storage, liquid/slurry separation.	
9. CROSS REFERENCE ID NUMBERS 02-01-03-01, 02-01-01-06.	
10. REFERENCES	
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract #68-02-1392, July 1975. 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA-625/6-74-003, Washington, 1974. B) BACKGROUND INFORMATION 186 Mitre Corporation, "Compendium of Analytical Methods, Vol. II, Method Summaries," U.S. Environmental Protection Agency, PB-228-425, April 1973. C) FIELD APPLICATIONS	

TITLE SEPARATION OF LIQUID/SLURRY SAMPLES (CONTINUED)

ID NO. 02-01-02-03

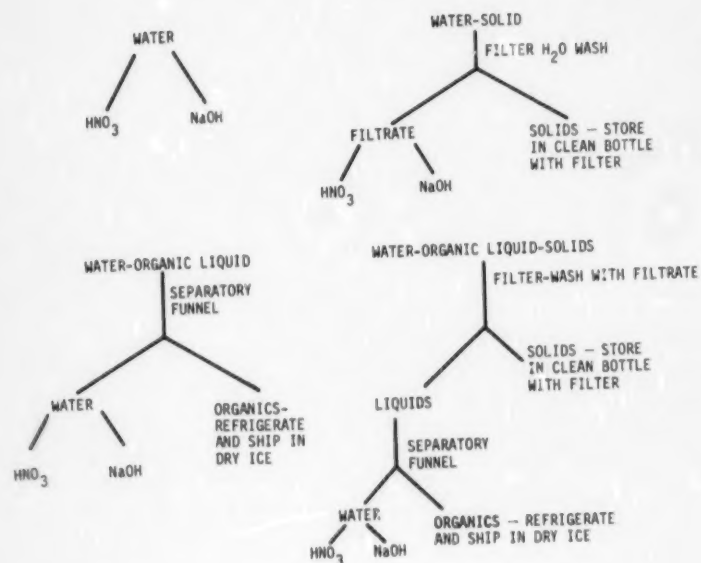


Figure 02-01-02-03A. Typical Separation Schemes for Process Liquids.

1. TITLE RECOMMENDATIONS FOR PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT		2. IDENTIFICATION CODE 02-01-03-01	
3. ABSTRACT OF METHODOLOGY			
Table 02-01-03-01A is a general summary of the preservation methods that are employed to retard change in the samples. Table 02-01-03-01B details methods of preservation that are intended to retard biological action, hydrolyses of chemical compounds and complexes, and to reduce volatility of constituents. This table also contains information concerning the normal volume required for a standard AIHA analytical analysis, as well as the type of storage container and the longest holding time possible in that container.			
4. APPLICATION: All levels.			
A) OPERATIONAL SCOPE These preservation techniques are designed to be used on samples of domestic sewage, industrial waste or natural waters. B) INTERFERENCES/LIMITATIONS Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inadvertently continue after the sample is removed from the parent source. The only solution to this problem is speedy analysis of the sample once it has been removed from the source. C) RECOMMENDED USE AREA These practices are recommended for all use areas.			
5. OPERATIONAL PARAMETERS			
A) RANGE These preservation techniques can be used to preserve trace to major components of the sample. B) ACCURACY N/A C) PRECISION N/A			
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED	
(See Table 02-01-03-01A and B)		(See Table 02-01-03-01A and B)	
8. KEYWORD INDEX: Analysis, sample preservation.			
9. CROSS REFERENCE ID NUMBERS			
10. REFERENCES			
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Waste," National Environmental Research Center, EPA 625/6-74-003, Washington, 1974. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water: Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, "Standard Methods of Sampling Industrial Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 2. C) FIELD APPLICATIONS			

**TITLE RECOMMENDATIONS FOR PRESERVATION OF SAMPLES ACCORDING
TO MEASUREMENT (CONTINUED)**

ID NO. 02-01-03-01

Table 02-01-03-01A. General Preservation Techniques (185).

Preservative	Action	Applicable to:
HgCl ₂	Bacterial Inhibitor	Nitrogen forms, phosphorus forms
Acid (HNO ₃)	Metals solvent, prevents precipitation	Metals
Acid (H ₂ SO ₄)	Bacterial Inhibitor	Organic samples (COD, oil and grease, organic carbon)
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration	Bacterial Inhibitor	Acidity-alkalinity, organic materials, BOD, color, odor, organic P, organic N, carbon, etc., biological organism (coliform, etc.)

TITLE RECOMMENDATIONS FOR PRESERVATION OF SAMPLES ACCORDING
TO MEASUREMENT (CONTINUED)

ID NO. 02-01-03-01

 Table 02-01-03-01B. Recommendation for Sampling and
Preservation of Samples According to Measurement (185).

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Acidity	100	P, G ⁽²⁾	Cool, 4°C	24 Hrs.
Alkalinity	100	P, G	Cool, 4°C	24 Hrs.
Arsenic	100	P, G	HNO ₃ to pH <2	6 Mos.
BOD	1000	P, G	Cool, 4°C	6 Hrs. (3)
Bromide	100	P, G	Cool, 4°C	24 Hrs.
COD	50	P, G	H ₂ SO ₄ to pH <2	7 Days
Chloride	50	P, G	None Req.	7 Days
Chlorine Req.	50	P, G	Cool, 4°C	24 Hrs.
Color	50	P, G	Cool, 4°C	24 Hrs.
Cyanides	500	P, G	Cool, 4°C NaOH to pH 12	24 Hrs.
Dissolved Oxygen				
Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	No Holding
Fluoride	300	P, G	Cool, 4°C	7 Days
Hardness	100	P, G	Cool, 4°C	7 Days
Iodide	100	P, G	Cool, 4°C	24 Hrs.
MBAS	250	P, G	Cool, 4°C	24 Hrs.
Metals				
Dissolved	200	P, G	Filter on site HNO ₃ to pH <2	6 Mos.
Suspended			Filter on site	6 Mos.
Total	100		HNO ₃ to pH <2	6 Mos.
Mercury				
Dissolved	100	P, G	Filter HNO ₃ to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P, G	HNO ₃ to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Nitrogen				
Ammonia	400	P, G	Cool, 4°C H ₂ SO ₄ to pH <2	24 Hrs. (4)
Kjeldahl	500	P, G	Cool, 4°C H ₂ SO ₄ to pH <2	24 Hrs. (4)
Nitrate	100	P, G	Cool, 4°C H ₂ SO ₄ to pH <2	24 Hrs. (4)
Nitrite	50	P, G	Cool, 4°C	24 Hrs. (4)
NTA	50	P, G	Cool, 4°C	24 Hrs.

TITLE RECOMMENDATIONS FOR PRESERVATION OF SAMPLES ACCORDING
TO MEASUREMENT (CONTINUED)

ID NO. 02-01-03-01

Table 02-01-03-01B. (Continued)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Oil & Grease	1000	G only	Cool, 4°C H ₂ SO ₄ to pH -2	24 Hrs.
Organic Carbon	25	P, G	Cool, 4°C H ₂ SO ₄ to pH -2	24 Hrs.
pH	25	P, G	Cool, 4°C Det. on site	6 Hrs. (3)
Phenolics	500	G only	Cool, 4°C H ₃ PO ₄ to pH -4 1:10 g CuSO ₄ /l	24 Hrs.
Phosphorus				
Ortho- phosphate, Dissolved	50	P, G	Filter on site Cool, 4°C	24 Hrs. (4)
Hydrolyzable	50	P, G	Cool, 4°C H ₂ SO ₄ to pH -2	24 Hrs. (4)
Total	50	P, G	Cool, 4°C	24 Hrs. (4)
Total, Dissolved	50	P, G	Filter on site Cool, 4°C	24 Hrs. (4)
Residue				
Filterable	100	P, G	Cool, 4°C	7 Days
Non- Filterable	100	P, G	Cool, 4°C	7 Days
Total	100	P, G	Cool, 4°C	7 Days
Volatile	100	P, G	Cool, 4°C	7 Days
Settleable Matter	1000	P, G	None Req.	24 Hrs.
Selenium	50	P, G	HNO ₃ to pH -2	6 Mos.
Silica	50	P only	Cool, 4°C	7 Days
Specific Conductance	100	P, G	Cool, 4°C	24 Hrs. (5)
Sulfate	50	P, G	Cool, 4°C	7 Days
Sulfide	50	P, G	2 ml zinc acetate	24 Hrs.
Sulfite	50	P, G	Cool, 4°C	24 Hrs.
Temperature	1000	P, G	Det. on site	No Holding
Threshold Odor	200	G only	Cool, 4°C	24 Hrs.
Turbidity	100	P, G	Cool, 4°C	7 Days

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 23, p. 72-91 (1973).
2. Plastic or Glass
3. If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.
4. Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/l, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.
5. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.
6. It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

1. TITLE PREPARING COAL SAMPLES FOR ULTIMATE AND/OR PROXIMATE ANALYSIS (MECHANICAL AND MANUAL REDUCTION AND DIVISION)	2. IDENTIFICATION CODE 02-01-03-02
3. ABSTRACT OF METHODOLOGY	
Figure 02-01-03-02A presents a flow diagram which summarizes the procedure of sample preparation for analysis. The recommended minimum sizes for initial reduction of the gross sample (collected using procedure of 01-03-01) are shown in Table 02-01-03-02A. The sample is then ground to pass a No. 4 mesh sieve (4.75 x 0 mm) as indicated in Table 02-01-03-02B. The sample is then divided using a large riffle (see Figure 02-01-03-02B for diagram of acceptable riffle sampler) to a quantity not less than shown in Table 02-01-03-02B, followed by further reduction to No. 8 mesh sieve with suitable pulverizing equipment. The subsample is then divided by riffling to not less than the quantity shown in Table 02-01-03-02B. Successive reductions and divisions are carried out until No. 60 mesh sieve is achieved. Mechanical dividers other than riffles, such as reciprocating or rotating cutters, rotating hoppers, etc., can also be used. When riffles or other mechanical devices are unavailable, samples can be reduced by manual coning and quartering methods, as illustrated in Figure 01-03-02-01A.	
4. APPLICATION: Environmental assessment.	
A) OPERATIONAL SCOPE The methods are applicable to all coal samples collected under 01-03-01, at ambient temperatures and pressures. B) INTERFERENCES/LIMITATIONS Proper use of the methods reflect consideration of the gas sample itself and of number and weight of increments required. Results are influenced by skill of the personnel involved and the care taken in the procedures employed. C) RECOMMENDED USE AREA This is the recommended procedure for the preparation of coal samples for all levels of analysis. Methods apply to all coals sampled by procedures cited in 01-03-01. See 02-02-01-03, 02-03-04, and 02-02-01-04.	
5. OPERATIONAL PARAMETERS	
A) RANGE Sample reduction and division depends on the range of the equipment (manual and automatic) used. B) ACCURACY 10% or better. C) PRECISION $\pm 10\%$ or better.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
N/A	Air drying oven (optional), gross sample scale, laboratory balance; crushers or grinders (jaw, cone, or rotary crusher or hammer mill); pulverizer or mill (porcelain-jar ball mill); mixing wheel; sieves; mortar and pestle; mechanical sample dividers, riffles, feed scoop, feed trough; laboratory sample containers.
8. KEYWORD INDEX: Sample preparation, solids, reduction/division, air drying, moisture.	
9. CROSS REFERENCE ID NUMBERS 01-03-01-02; 02-02-01-03; 02-02-01-04; 01-03-02-01; 02-03-04.	
10. REFERENCES	
A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2013-68, "Preparing Coal Samples for Analysis," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 323-336. 058 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Process Measurements, Lurgi Coal Gasification Process," EPA Contract No. 68-02-1412, March 1975. B) BACKGROUND INFORMATION 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2234, "Standard Methods for Sampling of Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 357-375. 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, E11, "Wire Cloth Sieves for Testing Purposes," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 431-435. 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D197-30, "Sampling and Fineness Test of Pulverized Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 10-12. 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D410-38, "Standard Method of Test for Sieve Analysis of Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 70-71.	

TITLE PREPARING COAL SAMPLES FOR ULTIMATE AND/OR PROXIMATE ANALYSIS
(MECHANICAL AND MANUAL REDUCTION AND DIVISION) (CONTINUED)

ID NO. 02-01-03-02

C) FIELD APPLICATIONS

186 Silverman, L., et al, "Particle Size Analysis in Industrial Hygiene," New York, Academic Press, 1971, p. 71.

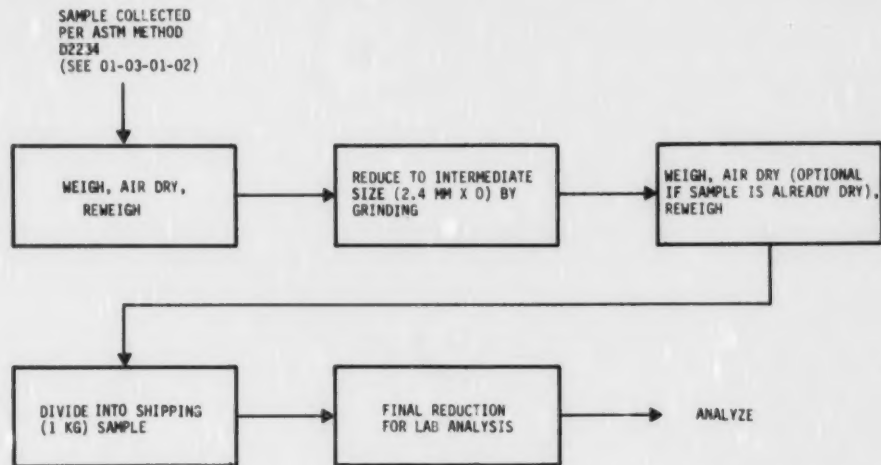


Figure 02-01-03-01A. Scheme for Preparation of Coal Samples for Analysis (From Reference 057).

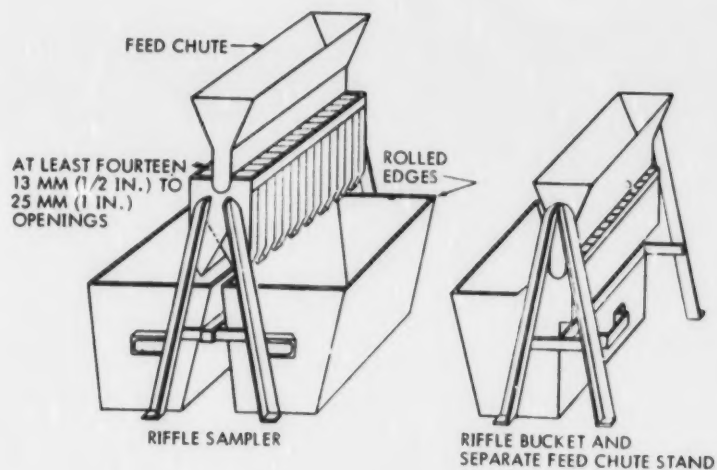


Figure 02-01-03-02B. Riffle Samplers (From Reference 057).

TITLE PREPARING COAL SAMPLES FOR ULTIMATE AND/OR PROXIMATE ANALYSIS
(MECHANICAL AND MANUAL REDUCTION AND DIVISION) (CONTINUED)

ID NO. 02-01-03-02

Table 02-01-03-02A. Size Reduction of Gross Sample* (Reference 057).

Material passing 100% through screen	Divide to a minimum weight of kg	
	Group A**	Group B***
5 - 15 cm (2 - 6 in.)	105 kg	245 kg
1.6 - 15 cm (5/8 - 2 in.)	45 kg	100 kg
1.6 cm (5/8 in.) and under	15 kg	35 kg

*Based on the data from Table 01-03-01-02A

**Mechanically cleaned coal

***All other coal

Table 02-01-03-02B. Preparation of Laboratory Samples (Reference 057).

Crush to pass at least 95% through sieve	Divide to a minimum weight of g*	
	Group A**	Group B***
No. 4 (4.74 mm)	2000	4000
No. 8 (2.36 mm)	500	1000
No. 20 (850 μ m)	250	500
No. 60 (250 μ m) (100% through)	50	50

*If a moisture sample is required, increase the quantity of No. 4 (4.75 mm) or No. 8 (2.36 mm) sieve subsample by 500 g

**Mechanically cleaned coal

***All other coals

1. TITLE SAMPLE RECOVERY FROM IMPINGERS		2. IDENTIFICATION CODE 02-01-03-03
3. ABSTRACT OF METHODOLOGY Upon completion of sampling by absorption in liquids contained in impingers, the contents of each impinger are returned quantitatively to individually labelled original solution bottles. Each liquid impinger is rinsed with 50 ml portions of high purity water; the rinsings are then combined with the catch. Concentrated nitric acid may be added to reduce the pH to between 1 and 2, in order to stabilize metal ions and to prevent formation of precipitates (hydroxides) and/or absorption of sample trace elements on container surfaces. Alternatively, sodium hydroxide can be added to stabilize anions. Following shipment to and receipt of the samples in the laboratory, the volumes of each of the solutions are measured using a clean graduated cylinder, and the solutions are then returned to the original containers. It is desirable to begin with the last impinger solution in the sampling train and to work toward the first solution which has the greatest concentration of trapped species. The graduated cylinder is rinsed between each solution measurement, and cleaned with nitric acid between series of solutions.		
4. APPLICATION: Environmental assessment, engineering evaluation R&D		
A) OPERATIONAL SCOPE Method is applicable to sample recovery of liquid impingers and pre-cooler trap, from flue gas and fugitive gas sampling.		
B) INTERFERENCES/LIMITATIONS Precipitate formation and trace element absorption on container walls may occur if low pH is not maintained in solutions.		
C) RECOMMENDED USE AREA This is the recommended procedure for sample recovery from impingers, including pre-cooler traps for environmental assessment and engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A		
B) ACCURACY N/A		
C) PRECISION N/A		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Concentrated nitric acid, reagent quality water.		Graduated cylinder, labeled solution bottles.
8. KEYWORD INDEX: Sample recovery, impingers.		
9. CROSS REFERENCE ID NUMBERS 01-05; 02-01-01-01, 02-01-01-05, 02-01-03-01.		
10. REFERENCES		
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract #68-02-1393, July 1975.		
B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1193-70, "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 196-7.		
C) FIELD APPLICATIONS		

1. TITLE REMOVAL OF FILTERS FROM FILTER HOLDERS	2. IDENTIFICATION CODE 02-01-03-04
3. ABSTRACT OF METHODOLOGY The filter must be carefully removed from the sampler in a clean, dust-free area using the following procedure. First, the filter holder is loosened, and the clamp frame is carefully removed from the surface of the filter. Using duct-bill tweezers, filter material adhering to the clamp frame is scraped onto the filter surface. Next, the tweezers are inserted under the filter (between the filter and filter support) and one inch (2.54 cm) of the outer boundary is folded toward the center. The filter is then folded in half, then in quarters (see Figure 02-01-03-01A). The folded filter is then placed in a labeled petri particulate-bearing filter and is dried at 105°C for three hours, cooled in a desiccator and weighed. Any particulate matter collected from liners, cyclone and cyclone wash are then transferred to the filter pad after they are individually weighed (see 02-01-03-05). The composite sample is ready for subsequent analysis by oxygen plasma ashing (see 02-01-04-02). The filter used in the high volume stack sampler (see 01-01-01-03) is removed from the housing using polyethylene gloves in a clean, dust-free environment and is then transferred to a polyethylene envelope for subsequent morphological analysis (see 02-04-01-03, 02-04-01-04, 02-04-02-03) or chemical analysis (02-02).	
4. APPLICATION: Environmental assessment, engineering evaluation R&D. A) OPERATIONAL SCOPE Method is applicable to all standard filters used in flue gas and fugitive gas sampling equipment. B) INTERFERENCES/LIMITATIONS Care must be taken to avoid loss of sample due to spillage, or sample contamination by dust, dirt, or equipment. C) RECOMMENDED USE AREA This procedure is used for environmental assessment and engineering evaluation R&D.	
5. OPERATIONAL PARAMETERS A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED Drying oven (to 105°C); desiccator; analytical balance.
8. KEYWORD INDEX: Filter, particulate, handling.	
9. CROSS REFERENCE ID NUMBERS 01-01-01-03; 02-01-04-02, 02-01-03-05, 02-01-03-06; 02-04-01-04, 02-04-01-03, 02-04-02-03.	
10. REFERENCES A) PRIMARY SOURCE 058 Hamersma, J.W., and S. Reynolds, "Tentative Procedures for Process Measurements; Lurgi Coal Gasification Process," EPA Contract No. 68-02-1412, TRW Systems, Inc., March 1975, p. 4-6. B) BACKGROUND INFORMATION 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract #68-02-1393, July 1975. 187 "Method 5: Determination of Particulate Emissions from Stationary Sources," Federal Register 36, No. 247, 24888-9, December 23, 1971. C) FIELD APPLICATIONS	

TITLE REMOVAL OF FILTERS FROM FILTER HOLDERS (CONTINUED)

ID NO. 02-01-03-04

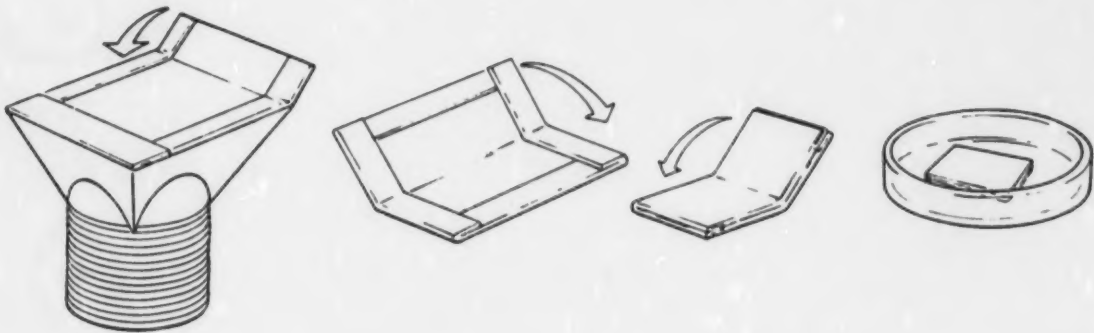


Figure 02-01-03-04-A. Folding Procedure for Particulate-Laden Filter from High Volume Air Sampler (Ref. 058).

1. TITLE REMOVAL OF PARTICULATE FROM CYCLONES	2. IDENTIFICATION CODE 02-01-03-06
3. ABSTRACT OF METHODOLOGY	
At the conclusion of sampling, sampled particulates are removed from cyclones using the following procedure. First, the heaters are turned off and the oven door is opened to cool the filter housing and cyclone parts. These components are then removed and the sample is quantitatively transferred to a labeled, preweighed nalgene bottle using antistatic nylon brushes or by tapping the sides of the cyclone. The contents of all the remaining connectors and transformers are then brushed and flushed with solvent (acetone) into separate labeled containers. In preparation for analysis, the dry particulate sample is dried for three hours at 105°C, cooled in a desiccator and weighed. The acetone rinse samples are evaporated to dryness on a steam bath, then cooled in a desiccator and weighed. All samples must be retained in their respective beakers. The samples are then combined with particulates collected on the high volume air sampler filter pad (see 02-01-03-04) and analyzed by suitable methods (e.g., microscopy, etc.). (See 02-01-04-02, 02-04-01-03, 02-04-01-04, 02-04-02-03.)	
4. APPLICATION: Environmental assessment, engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to all cyclones used in flue gas sampling. B) INTERFERENCES/LIMITATIONS Care must be taken to avoid sample loss due to spillage, or sample contamination by dust, dirt, etc. C) RECOMMENDED USE AREA This method is recommended for engineering evaluation R&D and environmental assessment.	
5. OPERATIONAL PARAMETERS	
A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Acetone (reagent grade or better).	Drying oven (to 105°C); desiccator; analytical balance.
8. KEYWORD INDEX: Cyclone, particulates, sample handling.	
9. CROSS REFERENCE ID NUMBERS 01-01-01-03; 02-01-03-04, 02-01-04-02; 02-04-01-03, 02-04-01-04, 02-04-02-03.	
10. REFERENCES	
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975. 093 Clausen, J., A. Grant, D. Moore and S. Reynolds, "Field Sampling for Cytotoxicity Test Samples Using a Series Cyclone Sampling Train," Interim Report, 17 March 1975 to 26 September 1975, EPA Contract No. 68-02-1412, TRW Systems, Inc., Appendix A. B) BACKGROUND INFORMATION 188 "Method 5: Determination of Particulate Emissions from Stationary Sources," Federal Register 36, No. 247, 24888-9, December 23, 1971. C) FIELD APPLICATIONS	

1. TITLE HANDLING OF PROBE LINER SAMPLES	2. IDENTIFICATION CODE 02-01-03-06
3. ABSTRACT OF METHODOLOGY The probe liner (Kapton) is removed from the probe, first using plastic tweezers to pull it out far enough to get a firm hand grip. Using polyethylene disposable gloves, the liner is pulled from the probe and gently rolled as it is removed; the roll is then placed in a pre-tared polyethylene bottle for weighing. Upon receipt in the laboratory, the liner is cut into smaller sections; each section is then rinsed with acetone into a pre-tared 250-ml beaker. The acetone and water are then evaporated on a steam bath; the beaker is then cooled in a desiccator, and the particulate weight is subsequently determined. The probe liner particulates are then combined with particulates collected on the HVSS filter pad (see 02-01-03-04) for subsequent preparation by plasma ashing (see 02-01-04-03) or other suitable techniques.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to all probe liner samples collected in flue gas sampling. B) INTERFERENCES/LIMITATIONS Samples must be protected from contamination by dust, dirt, etc., and loss due to spillage must be avoided. C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D procedure for the removal of particulates from probe liner samples.	
5. OPERATIONAL PARAMETERS	
A) RANGE N/A B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED Acetone	7. EQUIPMENT REQUIRED Steam bath; desiccator; 250-ml beaker; analytical balance.
8. KEYWORD INDEX: Probe liner sample, particulates, sample handling.	
9. CROSS REFERENCE ID NUMBERS 01-01-01-03; 02-01-03-04, 02-01-04-03.	
10. REFERENCES	
A) PRIMARY SOURCE 018 Flegal, C. A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975, n. 7-3. B) BACKGROUND INFORMATION 188 "Method 5: Determination of Particulate Emissions from Stationary Sources," Federal Register 36, No. 247, 24888-9, December 23, 1971. C) FIELD APPLICATIONS	

1. TITLE TOTAL CHLORINE IN COAL (ESCHKA ANALYSIS)	2. IDENTIFICATION CODE 02-01-04-01
3. ABSTRACT OF METHODOLOGY A weighed sample of coal, which is ground to pass a No. 60 mesh sieve, is mixed with Eschka mixture and burned in a bomb containing oxygen under pressure and a small amount of ammonium carbonate solution. Alternatively, a similar sample of coal is mixed with Eschka mixture and heated at $675 \pm 25^\circ\text{C}$ in an oxidizing atmosphere in a muffle furnace. The chlorides contained in the resultant ammonium carbonate solution or incinerated Eschka mixture are subsequently determined by potentiometric titration or a modified Volhard procedure (see 02-03-02-01).	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE The method is applicable to all sampled coals, coke and related materials (ground to pass a No. 60 mesh sieve) and is best performed by commercial analytical laboratories. B) INTERFERENCES/LIMITATIONS N/Q C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D procedure for the determination of total chlorine in coal and coke.	
5. OPERATIONAL PARAMETERS A) RANGE Methods have sensitivities of $\pm 10\%$ or less. B) ACCURACY 10% or better. C) PRECISION 0.03% chlorine for duplicate determinations performed in the same laboratory. 0.06% chlorine for duplicate determinations performed in different laboratories.	
6. REAGENTS REQUIRED Reagent water, ammonium carbonate, Eschka mixture (light calcined magnesium oxide with one part of anhydrous sodium carbonate), ferric ammonium sulfate indicator solution, nitric acid solution, nitrobenzene, oxygen, potassium thiocyanate (standard solution), silver nitrate (standard solution).	7. EQUIPMENT REQUIRED Laboratory balance, apparatus for bomb combustion of the sample, including oxygen bomb, capsule, firing wire, firing circuit, and metal vessel for bomb immersion in 2 liters of water; apparatus for Eschka combustion, including crucibles and muffle furnace; potentiometric titration assembly (see 02-03-02-01).
8. KEYWORD INDEX: Total chlorine analysis, coal, combustion, potentiometric titration.	
9. CROSS REFERENCE ID NUMBERS 02-03-02-01.	
10. REFERENCES A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels, Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2361-66, "Standard Method for Test for Chlorine in Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 376-78. B) BACKGROUND INFORMATION 057 ASTM Committee D-3 and D-5, "Gaseous Fuels, Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2015-66 "Standard Method of Test for Chlorine in Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, pp. 343-350. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, E200-67, "Standard Methods for Preparation, Standardization and Storage of Standard Solutions for Chemical Analysis," American Society for Testing and Materials, Philadelphia, PA., 1971. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1193, American Society for Testing and Materials, Philadelphia, PA., 1971.	

TITLE TOTAL CHLORINE IN COAL (ESCHKA ANALYSIS)

ID NO. 02-01-04-01

B) BACKGROUND INFORMATION

189 ASTM Committee E-1, et al, "General Test Methods," 1971 Annual Book of ASTM Standards, Part 30, E144-64, "Recommended Practice for Safe Use of Oxygen Combustion Bombs," pp. 287-288.

C) FIELD APPLICATIONS

1. TITLE COAL DISSOLUTION SCHEME FOR VARIOUS ELEMENTS		2. IDENTIFICATION CODE 02-01-04-02
3. ABSTRACT OF METHODOLOGY		
Figure 02-01-04-02A shows the recommended ashing and dissolution techniques for coal samples. Specific methods for individual elements and groups of elements are given. Recommended methods are also given for the final analysis. Prior to decomposition, the coal is ground to a minimum of 100 mesh in a ball mill. Particle size is verified using a nylon 100-mesh screen. Any particles which are not ground to the correct size in the ball mill are broken up with an agate mortar and pestle. Finally, the sample is dried at 50°C overnight.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE These procedures are designed to be used on any coal sample for the purpose of trace metal analysis. Low temperature plasma ashing is recommended because of its proven ability to prevent loss of volatile elements through vaporization. B) INTERFERENCES/LIMITATIONS Drying to constant weight may not be possible for a coal sample. Care must be taken to maintain cleanliness and the use of high purity reagents is important to limit blank values. C) RECOMMENDED USE AREA Engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE N/A B) ACCURACY N/Q (Normal retention values for these ashing techniques are better than 90%). C) PRECISION N/A		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
High purity nitric and hydrochloric acids, high purity sodium hydroxide, high purity sodium carbonate, high purity hydrofluoric acid.		Low temperature plasma asher (International Plasma Corporation Model 1001B or equivalent), muffle furnace.
8. KEYWORD INDEX: Coal, coal dissolution, ashing.		
9. CROSS REFERENCE ID NUMBERS 02-01-03-02; 02-02-01-05; 02-01-01, 02-01-04-03.		
10. REFERENCES		
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975. B) BACKGROUND INFORMATION C) FIELD APPLICATIONS 025 Flegal, C., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Final Report of Measurement Techniques for Inorganic Trace Materials in Control Systems Streams," TRW Defense and Space Systems, Redondo Beach, California, EPA Contract No. 68-02-1393, in press.		

TITLE COAL DISSOLUTION SCHEME FOR VARIOUS ELEMENTS (CONTINUED)

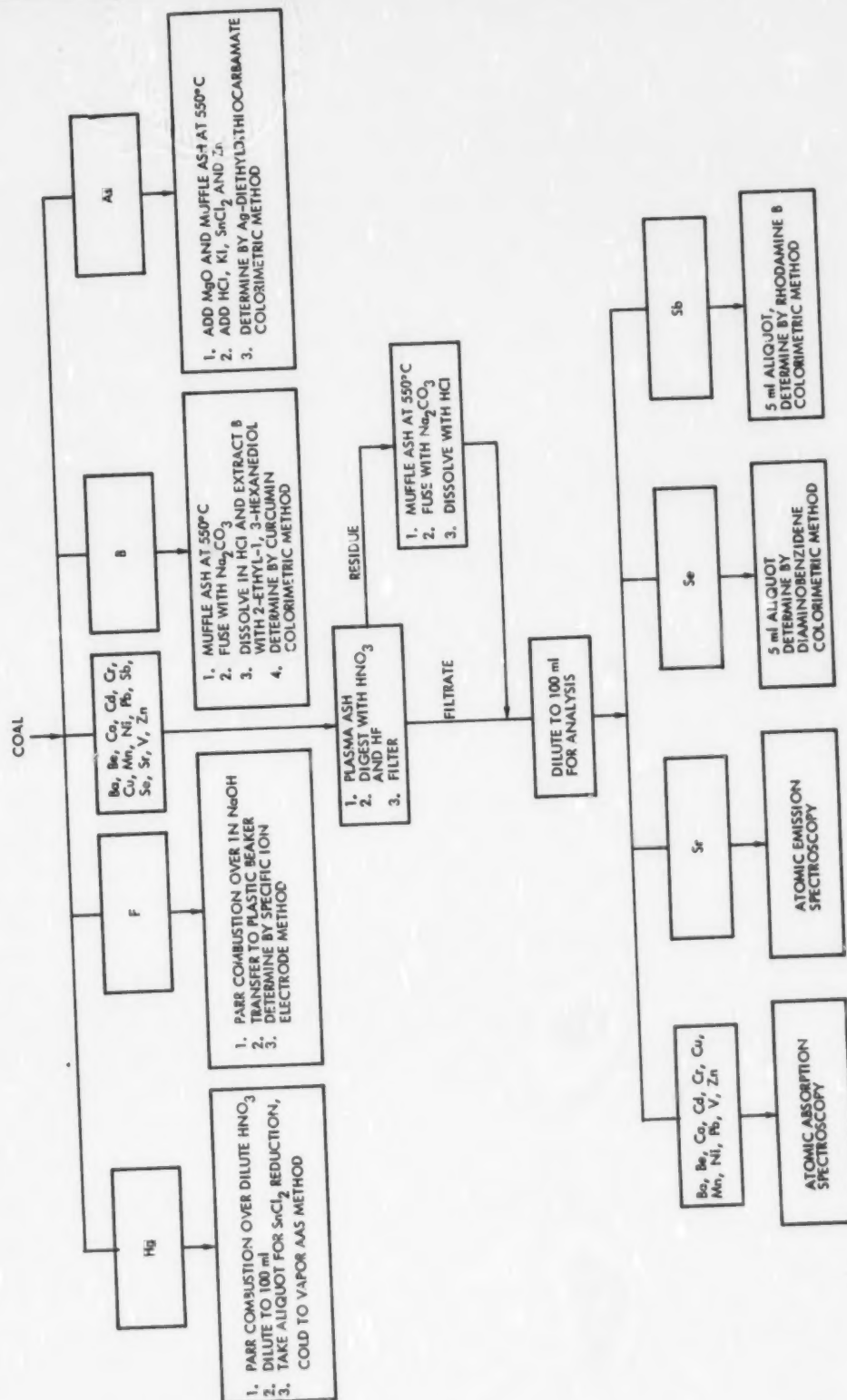


Figure 02-01-04-02A. Specialized Coal Dissolution and Analysis Scheme.

1. TITLE LOW TEMPERATURE PLASMA ASHING AND DISSOLUTION OF COLLECTED PARTICULATE		2. IDENTIFICATION CODE 02-01-04-03
3. ABSTRACT OF METHODOLOGY		
The composite particulate samples on the filter are placed in a large petri dish and oxygen plasma ashed for 4 hours. The samples are then removed, transferred to pre-cleaned, covered 250-ml beakers, and digested for 2 hours in 40 ml constant boiling aqua regia solution (8 ml 19% HCl + 32 ml 40% HNO₃). The solutions are filtered through No. 41 Whatman filter paper into 100-ml Nalgene volumetric flasks. If appreciable residue remains, it can be recombined with the original filtrates by ashing at 550°C and fusing with a small amount of Na₂CO₃ (~ 10 parts Na₂CO₃ to 1 part residue), followed by re-dissolution with 1:1 HCl. In all cases when trace elements are to be determined high purity reagents, such as J.T. Baker Ultrex Brand, are to be used (see 02-01-01-06).		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE This procedure is applicable to all particulates collected from probe liner, filter or cyclones. This procedure can also be used on solid samples that are ground to less than 100 mesh. B) INTERFERENCES/LIMITATIONS This method is primarily designed to dissolve flyash or other particulates from process sources. Geological samples might require more strenuous wet ashing. C) RECOMMENDED USE AREA Engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE Trace quantities. B) ACCURACY Better than 95% recovery for most elements. C) PRECISION N/Q (±10%).		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
High purity HCl, HNO ₃ , Na ₂ CO ₃ .		Plasma Asher (International Plasma Corp. Model 1001B or equivalent), Nalgene labware, muffle furnace.
8. KEYWORD INDEX: Analysis, plasma ashing, particulate dissolution.		
9. CROSS REFERENCE ID NUMBERS 02-01-04-03, 02-01-01-06.		
10. REFERENCES		
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975. B) BACKGROUND INFORMATION C) FIELD APPLICATIONS 025 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich, and C. Zee, "Final Report for Measurement Techniques for Inorganic Trace Materials in Control Systems Streams," TRW Defense and Space Systems, Redondo Beach, California, EPA Contract No. 68-02-1393, in press.		

1. TITLE MIXED LIGAND EXTRACTION OF Ag, Cd, Co, Cu, Fe, Ni, Pb, Zn AND Be FROM TAPE SAMPLER DUST SPOTS	2. IDENTIFICATION CODE 02-01-04-04
3. ABSTRACT OF METHODOLOGY Dust spots collected on filter tape (see 01-06-01-07) or high volume (see 01-06-01-05) samplers are extracted with a mixed ligand system to remove the metals. An aliquot of the filter or the entire dust spot (normally 2.54 cm (1 inch) in diameter) is placed in a beaker and 2 ml of 15% ammonium acetate is added to adjust the pH (5-7). The $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is followed by 20 ml of an ethyl propionate solution of mixed ligands (0.1 g diphenylthiocarbazone, 0.75 g 8-quinolinol and 20 ml acetyl acetone made up to 100 ml with ethyl propionate). The solution is allowed to equilibrate and then directly aspirated into an atomic absorption spectrophotometer or ICPOES for analysis (see 02-02-01-05 or 02-03-02-01). Standards are added to unused filters and extracted in the same manner.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE This method of extracting Ag, Cd, Co, Cu, Fe, Ni, Pb, Zn and Be can be used on samples of ambient particulates collected on glass fiber or acid-washed filter paper. The best results are obtained with acid washed filter paper. If metal sulfides are present, the sample is exposed to bromine vapors for 10 minutes (5" $\rightarrow$ 50"). B) INTERFERENCES/LIMITATIONS This procedure reduces interferences and sample blanks by direct extraction. Under nonstandard conditions (other than common salts, sulfides) the efficiency of the extraction can vary. Also, this method is limited to the 9 metals discussed. C) RECOMMENDED USE AREA This method is applicable for fugitive emission analysis for engineering R&D.	
5. OPERATIONAL PARAMETERS	
A) RANGE Depending on the metal, between 2 to 120 μg of the element can be present without the need for dilution. B) ACCURACY ± 10 to 20%. C) PRECISION N/Q ($\pm 10\%$ estimated).	
6. REAGENTS REQUIRED Ammonium acetate, ethyl propionate, diphenylthiocarbazone, 8-quinolinol, acetyl acetone, bromine.	7. EQUIPMENT REQUIRED Tape sampler, lab glassware, atomic absorption spectrophotometer.
8. KEYWORD INDEX: Analysis, separation, mixed ligand.	
9. CROSS REFERENCE ID NUMBERS 01-06-01-05, 07: 02-02-01-05, 02-03-02-01.	
10. REFERENCES	
A) PRIMARY SOURCE 190 West, P.W., "The Determination of Trace Metals in Air," in "Determination of Air Quality," edited by Gleb Hamantov and W.D. Shults, New York, Plenum Publishing Corporation. B) BACKGROUND INFORMATION 191 Sachdev, S.L., and P.W. West, <u>Environ. Sci. Tech.</u>, 4, 749 (1970). C) FIELD APPLICATIONS	

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02-02-01 Single Element/Cation Analysis

- 02-02-01-01 Lead Analysis by Dithizone Colorimetric Procedure
- 02-02-01-02 Determination of Hg in Iodine Monochloride Impinger Solutions
- 02-02-01-03 Ultimate Analysis of Coal (for Carbon and Hydrogen, Nitrogen and Oxygen)
- 02-02-01-04 Analysis of Coal and Coke Ash for Al, Si, Fe, Ti, P, Ca, Na by Photometry and/or Chelatometric Titration
- 02-02-01-05 Atomic Absorption Techniques for Ba, Be, Cd, Ca, Cr, Cu, Pb, Mn, Hg, Ni, V, Zn, Al, Sb, As, Co, Fe, Mg, Mo, K, Ag, Na, Th, Sn, Ti
- 02-02-01-06 Determination of Acidity by Electrostatic Titration
- 02-02-01-07 Determination of Arsenic by Silver Diethyl Dithiocarbamate Method
- 02-02-01-08 Determination of Biochemical Oxygen Demand Using Bioassay Procedures
- 02-02-01-09 Determination of Dissolved Oxygen (Modified Winkler With Full Bottle Technique)
- 02-02-01-10 Determination of Dissolved Oxygen (DO) by Electrode (Probe) Method
- 02-02-01-11 Determination of Boron by Curcumin Method
- 02-02-01-12 Determination of Calcium by Titrimetry
- 02-02-01-13 Determination of Total Residual Chlorine by Amperometric Titration or Iodometric Titration
- 02-02-01-14 Determination of Silica (Dissolved)
- 02-02-01-15 Spectrophotometric Determination of Antimony
- 02-02-01-16 Determination of Selenium by Diaminobenzidine Method
- 02-02-01-17 Determination of Selenium by Distillation-Diaminobenzidine Method
- 02-02-01-18 Determination of Cations Using Specific Ion Electrodes (SIE)
- 02-02-01-19 Determination of Ammonia by Colorimetric Phenate Method
- 02-02-01-20 Determination of Total Nitrogen by Kjeldahl Method
- 02-02-01-21 Determination of Heavy Metals by Dithizone Method
- 02-02-01-22 Determination of Hexavalent Chromium by Diphenyl Carbazide Method
- 02-02-01-23 Determination of Iron (Total, Filterable, or Ferrous) by Phenanthroline Method
- 02-02-01-24 Determination of Chemical Oxygen Demand
- 02-02-01-25 Determination of Ammonia by Distillation Procedure
- 02-02-01-26 Determination of Beryllium by Aluminon Method
- 02-02-01-27 Determination of Total Chromium by Diphenyl Carbazide Method
- 02-02-01-28 Determination of Total Copper by Neocuproine Method
- 02-02-01-29 Determination of Calcium by Gravimetric Method
- 02-02-01-30 Determination of Total Magnesium by Gravimetric Method
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- 02-02-01-32 Determination of Potassium by Cobaltinitrite Method
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- 02-02-02 Multielement Analysis
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- 02-02-02-02 X-Ray Fluorescence of Environmental Samples
- 02-02-02-03 Optical Emission Spectroscopy (DC Arc/AC Spark)
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APPLICATION MATRIX FOR 02-02 ELEMENTAL ANALYSIS

METHOD	LEVEL 1 ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
02-02-01-01	●		●
02-02-01-02	●	●	●
02-02-01-03			●
02-02-01-04			●
02-02-01-05		●	●
02-02-01-06	●	●	
02-02-01-07	●		●
02-02-01-08	●	●	
02-02-01-09	●	●	
02-02-01-10	●	●	
02-02-01-11	●	●	
02-02-01-12		●	
02-02-01-13	●	●	
02-02-01-14	●	●	
02-02-01-15	●		
02-02-01-16	●		
02-02-01-17	●		
02-02-01-18	●		
02-02-01-19		●	
02-02-01-20		●	
02-02-01-21			●
02-02-01-22	●		●
02-02-01-23	●		●
02-02-01-24	●	●	
02-02-01-25	●	●	
02-02-01-26			●
02-02-01-27		●	
02-02-01-28		●	
02-02-01-29			●
02-02-01-30		●	
02-02-01-31		●	
02-02-01-32			●
02-02-01-33		●	
02-02-01-34	●	●	
02-02-01-35	●	●	
02-02-01-36		●	●
02-02-01-37		●	
02-02-02-01			●
02-02-02-02			●
02-02-02-03			●
02-02-02-04			●
02-02-02-05			●
02-02-02-06	●		
02-02-02-07	●		

ELEMENTAL ANALYSIS- ID No. 02-02

The abstracts presented in this section discuss the procedure categories of (02-02-01) single element/cation analysis and (02-02-02) multielement analysis. The methods employed for single element and cation analysis are spectrophotometry, atomic absorption spectroscopy, bioassay, specific ion electrodes, and volumetric, chelatometric, and electrometric (amperometric and potentiometric) titration methods. Specific procedures are recommended for each element or cation discussed. The techniques employed for multielement analysis include optical emission spectroscopy (inductively coupled plasma, DC arc, AC graphite spark), x-ray fluorescence, differential pulse anodic stripping, instrumental neutron activation analysis, and spark source mass spectrometry.

02-02-01 Single Element/Cation Analysis (Abstracts 02-02-01-01 through 02-02-01-23)

Spectrophotometric methods (02-02-01-01, 02, 03, 04, 07, 11, 14, 15, 16, 17, 19, 21, 22, 23), specific ion electrodes (02-02-01-18) electrode probes (02-02-01-10), potentiometric, chelatometric and volumetric titrations (02-02-01-04, 06, 09, 12, 13, 20) are commonly used in the analysis of single elements and cations. Some important factors which must be considered in the proper application of most of these methods are discussed in the introduction to Section 02-03 of this manual.

In addition to volumetric, potentiometric, and chelatometric titrations, amperometric (02-02-01-13) titrations can also be used. This technique is primarily used in precipitation reactions, although redox and chelatometric reactions may also be determined by amperometric titrations. In order to obtain a sharp endpoint in precipitation titration curves, however, the solubility of the precipitate cannot be high. This can be avoided by adjustment of the solvent used in order to limit the solubility of the product.

Atomic absorption spectroscopy (AAS) is one of the more sensitive methods for quantitative identification of a wide range of elements and cations. Some important considerations to the proper use of atomic absorption spectroscopy include the type or source of lamp to be used, the use of suitable fuel and oxidant, and optimum concentrations for standard solutions.

A variety of technical and commercial literature is currently available which gives specific procedures and optimum operating conditions for cations and elements (reference 193). The scope of AAS has recently been extended by the use of microprocessor-based computer instruments, which make high precision analyses on both major and minor constituents in the same sample possible. Two major advantages which are characteristic of the microprocessor technique are a signal integration capability, which significantly improves analytical precision, and an automatic calibration capability, using multiple standards for the handling of wide ranges of concentration in the same sample with good precision (reference 193).

The BOD procedure (02-02-01-08) which is used in the determination of biochemical oxygen demand (BOD) is an empirical method which measures the dissolved oxygen consumed by microbial life while oxidizing the organic matter present. Although high precision can be achieved using this technique, there is no acceptable method for determining accuracy. Additional information relating to the oxygen demand characteristics of samples may be obtained by applying specific samples (usually liquids or slurries).

Actual determinations of the dissolved oxygen present in the sample involves use of probe methods (membrane or thallium probes). Some important factors in the performance of membrane probes include concentration of dissolved inorganic salts and reactive species, and temperature. Broad variations in the kinds and concentrations of salts in the sample can impair the accuracy obtained, particularly when membrane probes are used. Certain gases (chlorine, hydrogen sulfide) which can pass through the membrane may also interfere. Chlorine may depolarize the cathode and cause a high probe output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfate ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place. The performance of membranes is generally not affected by pH changes, but membrane probes are temperature sensitive.

02-02-02 Multielement Analyses (Abstracts 02-02-02-01 through 02-02-02-07)

Methods used in multielement analysis include optical emission spectroscopy, including inductively coupled plasma OES (02-02-02-01), and DC arc/AC spark OES (02-02-02-03), X-ray fluorescence (02-02-02-02), anodic stripping voltammetry (02-02-02-04), instrumental neutron activation analysis (02-02-02-06) and spark source mass spectrometry (02-02-02-07 and -08).

Table 02-02-A lists some performance characteristics of most of these methods as applied to trace metal analysis, including the range of elements which can be examined, and selection criteria which can be applied to their usage. Table 02-02-B compares the screening capability of several multielement methods.

The methods generally function in either of two ways: by analyzing a given sample for a number of elements simultaneously (e.g., OES, SSMS, INAA) or by analyzing a sample for a number of elements consecutively, without manual adjustment (e.g., XRF). One determining factor in the choice of techniques is the availability of the instrument to the user, since the equipment is generally complex and not readily available. In many cases, extensive preparation of the sample will be required prior to actual analysis.

Interferences are generally encountered in applying the techniques to specific matrices. Special handling procedures such as plasma ashing, standard addition, dilution, or concentration steps are often required. Because the techniques are sensitive to very low or trace levels of elements, high purity reagents should be used in laboratory sample preparations.

Spark source mass spectrometry (02-02-02-06 and -07) is perhaps one of the most sensitive and universal techniques which is available for inorganic analysis. Matrix effects are important to accurate determinations. Samples high in organic content require ashing prior to analysis.

OES (02-02-02-01, -03) is an acceptable alternative to SSMS. Although the sensitivity of the method is less than SSMS, OES is more widely available. XRF (02-02-02-02) is less sensitive than either SSMS or OES. However, little or no pretreatment is required for samples when XRF is used. Moreover, the technique is nondestructive. The sensitivity of the INAA technique

Analytical Technique	Analytically Useful Elemental Range	Availability	Accuracy Capability	Sample Preparation	Cost Effectiveness	Analysis Time
Emission Spectroscopy						
DC Arc/AC Spark	Li to U	High	Acceptable	Moderate	Excellent	Medium
Inductively Coupled Plasma O.E.S.	Be to U	Low	Good	Minimal	Excellent	Short
X-Ray Fluorescence	Na to U	Intermediate	Acceptable	Moderate	Good	Medium
Electrochemical Methods						
Anodic Stripping Voltammetry	Pb, Cd, As, Cr, Se, Mn, Sn, Zn, Tl, Co, Cu, Fe, Hg, Sb, Al, Ni, Ag	High	Good	Minimal	Good	Medium
Nuclear Methods						
INAA*	H to U	Low	Good	Minimal	Excellent	Protracted
Mass Spectroscopic						
Spark Source	H to U	Low	Poor-Acceptable	Moderate	Excellent	Medium

*Instrumental Neutron Activation Analysis

Table 02-02-A. Summary of Multielement Analytical Technique Performance for Trace Material Sample Analysis.

TECHNIQUE	MULTI ELEMENT CAPABILITY	ACCURACY	SENSITIVITY	MATRIX			COST
				COAL	FLY ASH	WATER	
EMISSION SPECTROSCOPY DC ARC/AC SPARK (OES)	UNABLE TO RUN Hg, Se, Sb, F	±30-50% SEMIQUANT. ±10% QUANT.	GENERALLY ACCEPTABLE, VARIES WITH MATRIX	REMOVAL BY ASHING OF ORGANIC MATRIX	NONE NECESSARY	EVAPORATION	\$35.00/SAMPLE SEMIQUANT.
APOES *	ANY ELEMENTS TO A MAX. OF 50 PRESET AT FACTORY TO USERS SPECS	±40% SEMIQUANT. ±10% QUANT.	BETTER THAN AAS FOR ALL ELEMENTS	ASH, FOLLOWED BY ACID DISSOLUTION	ACID DISSOLUTION	NONE NECESSARY	\$14.00/SAMPLE
X-RAY FLUORESCENCE (XRF)	UNABLE TO RUN Li, Be, B	QUALITATIVE TO ±10% DEPENDING ON ELEMENT AND MATRIX	VARIABLE, DEPENDS ON ELEMENT AND MATRIX	CAN BE RUN DIRECT AFTER GRINDING AND BRICKETTING	GRIND AND BRICKET	RUN DIRECT	\$50.00/SAMPLE QUALIFICATION SAMPLE
INSTRUMENTAL NEUTRON ACTIVATION (INAA)	Be CANNOT BE DONE	±30% SEMIQUANT. 2-3% QUANT.	ACCEPTABLE, VARIES WITH MATRIX	NONE NECESSARY	NONE NECESSARY	NONE NECESSARY	\$325.00/SEMIQUANT. \$35.00/ELEMENT/ SAMPLE QUANT.
SPARK SOURCE MASS SPEC (SSMS)	ALL ELEMENTS CAN BE DETER- MINED	100-300% "QUICK AND DIRTY" ±30% SEMIQUANT.	ACCEPTABLE	REMOVE ORGANIC BY ASHING	NONE NECESSARY	EVAPORATION	\$45.00/SAMPLE ±100-300% \$225.00/SAMPLE SEMIQUANT.

* INDUCTIVELY COUPLED ARGON PLASMA OPTICAL EMISSION SPECTROSCOPY

Table 02-02-B. Screening capability of Several Multielement Techniques.

varies for different elements. The sensitivity depends upon the intensity of the activating source and the capacity of a specific element to absorb neutrons. For some elements (In, Re, Ir, Sm, Eu, Dy, Ho, Lu, V, As, Sb) activation analysis has greater sensitivity than chemical methods; for others (Fe, Ca, Pb, Bi, Zn, Cd, Na, K) INAA is less than or equal to chemical methods.

REFERENCES

- 192 Ewing, G.W., "Instrumental Methods of Chemical Analysis," New York, McGraw-Hill Book Co., 1960.
- 193 Perkin-Elmer Corporation, "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin-Elmer Corporation, May 1966.
- 194 Fernandez, F.J., and J.D. Kerber, "High-precision Analyses by Atomic Absorption," Am. Lab., 49, March 1976.
- 195 Barnett, W.B., and J.D. Kerber, Am. Lab., 7(8), 43 (1975).
- 196 Orion Research, "Analytical Methods Guide," Orion Research, Inc., 7th ed., Cambridge, Mass., May 1975.
- 197 Radian Corporation, "Sampling and Analytical Strategy for Potentially Hazardous Compounds in Petroleum Refinery Streams," Radian Corporation, Austin, Texas.
- 198 Harrison, W.W., G.G. Clemenas and C.W. Magee, J. Assoc. Offic. Anal. Chem., 54, 929 (1971).
- 199 Brown, R., M.L. Jacobs and H.E. Tayler, Am. Lab., 4(11), 29 (1972).

1. TITLE LEAD ANALYSIS BY DITHIZONE COLORIMETRIC PROCEDURE	2. IDENTIFICATION CODE 02-02-01-01
3. ABSTRACT OF METHODOLOGY Particulate lead is digested with nitric and perchloric acids. Vaporous lead collected on activated charcoal is extracted with aqua regia for 16 hrs at a temperature of 90 to 100°C. The carbon is removed by filtration prior to analysis. To these solutions a reducing/buffer (citrate-cyanide hydroxylamine-ammonium hydroxide), and dithizone in carbon tetrachloride are added. The lead is extracted into the carbon tetrachloride phase and the absorbance of the CCl₄/dithizone is read at 510 nm.	
4. APPLICATION: Engineering evaluation R&D, level 1 environmental assessment.	
A) OPERATIONAL SCOPE This method covers the determination of low levels of atmospheric lead. This method is primarily used for samples collected as particulate lead on filters or vaporous lead on activated charcoal and is not meant to be used directly for wastewater streams or process waters. B) INTERFERENCES/LIMITATIONS Dithizone gives colored complexes with bismuth, stannous tin, monovalent thallium, and indium; the procedures stated in this method reduce the interferences due to those four metals. Only in cases where the analyst suspects large quantities of these interfering ions should extra precautions be taken. Glassware used in this method must be of borosilicate glass and delead by soaking in warm nitric acid followed by rinsing with several portions of distilled water. C) RECOMMENDED USE AREA Engineering evaluation R&D testing for lead fugitive emissions.	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.001 to 1 ppm (estimated). B) ACCURACY ±10% (estimated). C) PRECISION ±10% (estimated).	
6. REAGENTS REQUIRED High purity water, buffer solution (dibasic ammonium citrate, hydroxylamine hydrochloride, potassium cyanide, and ammonium hydroxide), EDTA, dithizone, hydrochloric acid, lead nitrate, nitric acid, perchloric acid. (Note: All acids should be of high purity, see 02-01-01-06.)	7. EQUIPMENT REQUIRED Absorbance cell (200 ml capacity modified), spectrophotometer, automatic dispensing burets.
8. KEYWORD INDEX: Analysis, lead analysis, dithizone.	
9. CROSS REFERENCE ID NUMBERS 01-05-02-02; 02-01-01-06.	
10. REFERENCES	
A) PRIMARY SOURCE 053 ASTM, "Lead in the Atmosphere by Colorimetric Dithizone Procedure," 1974 Book of ASTM Standards, Part 26, D3112-72T, American Society for Testing and Materials, Philadelphia, PA., 1974, p. 633. B) BACKGROUND INFORMATION 200 Synder, L.J., <i>Anal. Chem.</i>, 39, 591 (1967). 201 Synder, L.J., <i>Anal. Chem.</i>, 19, 684 (1947). 202 Henderson, F.R., and L.J. Synder, <i>Anal. Chem.</i>, 31, 2113 (1959). C) FIELD APPLICATIONS	

2. IDENTIFICATION CODE

1. TITLE DETERMINATION OF Hg IN IODINE MONOCHLORIDE IMPINGER SOLUTIONS

02-02-01-02

3. ABSTRACT OF METHODOLOGY

Gaseous emissions are sampled from the stationary sources and collected in an iodine monochloride solution. The mercury collected (in the mercuric state) is reduced to elemental mercury in basic solution by the addition of hydroxylamine sulfate. Mercury is vaporized from the solution using a zero grade air stream and passed through a cylindrical gas cell (approximately 3.8 cm OD x 18 cm, see Figure 02-02-01-02A) with quartz windows. This gas cell is mounted in the burner area (without the flame) of the AAS. The internal optics of the AAS are used to monitor the absorption of the 253.7 nm line of the AAS hollow cathode lamp. Both blanks (any unused ICl solution) and standards are run in solutions containing ICl.

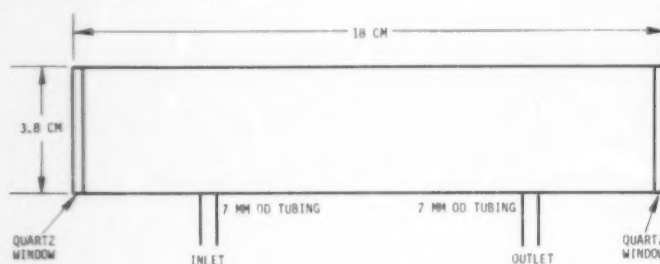


Figure 02-02-01-02A. Gas Cell Schematic (019).

4. APPLICATION: Compliance, engineering evaluation R&D, environmental assessment.

A) OPERATIONAL SCOPE

This method is specifically used for the determination of mercury in the ICl impinger solutions (see 01-01-01-02). This chemical system can also be used for other solutions containing mercuric salts.

B) INTERFERENCES/LIMITATIONS

Iodine monochloride is a very caustic and messy solution to handle in the field. Typically, iodine vapor escapes from the impingers and is passed through the train. While iodine monochloride must be used for compliance testing, a silver catalyzed persulfate solution provides an efficient and easily handled solution for trapping volatile metals and mercury in particular (see 01-01-01-02). Furthermore, the ammonium persulfate solution does not give a large background signal to the AAS analysis.

C) RECOMMENDED USE AREA

Compliance testing for Hg in flue gas stream.

5. OPERATIONAL PARAMETERS

A) RANGE 0.1 ppm of mercury can be determined in the impinger solutions.

B) ACCURACY N/Q ($\pm 15\%$ estimated).

C) PRECISION N/Q ($\pm 10\%$ estimated).

6. REAGENTS REQUIRED

Potassium iodine, hydrochloric acid, potassium hydroxide, distilled water, iodine monochloride, glass fiber filter (MSA-1106BH or equivalent), nitric acid, silica gel, soda lime, sodium hydroxide, mercuric chloride, hydroxylamine sulfate, sodium chloride.

7. EQUIPMENT REQUIRED

Atomic absorption spectrophotometry (Perkin-Elmer Model 303 or equivalent), balance, gas cell (see Figure 02-02-01-02A).

8. KEYWORD INDEX: Sampling, mercury sampling.

9. CROSS REFERENCE ID NUMBERS 01-01-01-02; 01-04-01-01.

10. REFERENCES

A) PRIMARY SOURCE

019 U. S. Environmental Protection Agency, Federal Register 36, No. 234, p. 23243, 1971.

B) BACKGROUND INFORMATION

020 Martin, R.M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, APT-0581.

021 Smith, W.S., et al, "Stack Gas Sampling Improved and Simplified with New Equipment", APCA Paper No. 67-119, 1967.

022 Hatch, W.R., and W.L. Ott, "Determination of Submicrogram Quantities of Mercury by Atomic Absorption Spectrophotometry," Anal. Chem., 40, 2085 (1968).

C) FIELD APPLICATIONS

TITLE DETERMINATION OF Hg IN IODINE MONOCHLORIDE IMPINGER SOLUTIONS (CONTINUED)

ID NO. 02-02-01-02

10. REFERENCES (Continued)

b) BACKGROUND INFORMATION (Continued)

- 023 Rome, J.J., "Maintenance Calibration and Operation of Isokinetic Source Sampling Equipment," EPA, APTD E-05-76.
- 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Book of ASTM Standards, Part 23, D 2928-71, "Standard Method for Sampling Stacks for Particulate Matter," American Society for Testing and Materials, Philadelphia, PA., 1971.

1. TITLE ULTIMATE ANALYSIS OF COAL (FOR CARBON AND HYDROGEN, NITROGEN AND OXYGEN)	2. IDENTIFICATION CODE 02-02-01-03
3. ABSTRACT OF METHODOLOGY	
The determination of carbon and hydrogen is made by complete oxidation of sample (see 01-03-01-02 and 02-01-03-02 for sample collection and preparation procedures) in a closed combustion tube which is packed with materials for the removal of interfering species. A typical tube is packed with sections of cupric oxide and lead chromate. The products of the combustion are then fixed in an absorption train consisting of a water absorber (solid dehydrating agent), a solid carbon dioxide absorber, and a guard tube which is packed with equal volumes of water absorbent and solid carbon dioxide absorbent. The percent carbon and hydrogen is then calculated from an increase in weight of the tubes. The determination of nitrogen is performed by the Kjeldahl-Gunning method, involving conversion of nitrogen into ammonium salts followed by decomposition of the salts and subsequent distillation of liberated ammonia into a sulfuric acid solution and back-titration of excess acid. An alternative method for nitrogen determination involving distillation of the ammonia into a solution of boric acid rather than sulfuric acid can be used. The percent oxygen in the sample is not measured directly but is calculated by subtracting the percent of H, C, N, S, moisture and ash from the sample.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to analysis of solid samples (coal, coke) collected from process streams. B) INTERFERENCES/LIMITATIONS Oxides of sulfur can interfere with C and H analyses, unless adequate combustion tube packings are used (cupric oxide, and lead chromate or silver). Also, oxides of nitrogen formed during the combustion procedures may lead to high results for carbon. There are no known interferences to nitrogen or oxygen determinations. C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D procedure for the ultimate analysis of coal and coke for carbon and hydrogen, nitrogen and oxygen.	
5. OPERATIONAL PARAMETERS	
A) RANGE Method gives the total percentages of carbon and hydrogen in the coal, including carbonate carbon, and hydrogen in moisture and in water of hydration of silicates. Method also gives total oxygen and nitrogen. B) ACCURACY N/Q C) PRECISION Permissible percentage differences in results obtained by the same laboratory include: Carbon - 0.3; Hydrogen - 0.07; Nitrogen - 0.05.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
For carbon and hydrogen determination: oxygen, cupric oxide, lead chromate, silver gauze, copper gauze, water absorbent (anhydrous magnesium perchlorate), carbon dioxide absorbent (sodium or potassium hydroxide in an inert carrier). For nitrogen determination: alkali solution (potassium sulfide/sodium hydroxide), ethyl alcohol, mercury, potassium permanganate, potassium sulfate, sucrose, sulfuric acid, zinc and for Kjeldahl-Gunning Method, methyl red indicator; for alternate method, boric acid solution.	For carbon and hydrogen determination: oxygen purifying train, consisting of first water absorber, carbon dioxide absorber, and guard tube; flow meter, combustion unit consisting of 3 furnace sections, combustion tube, combustion boat. For nitrogen determination: digestion unit, distillation unit, condenser, Kjeldahl digestion flask, Kjeldahl connecting bulb, Erlenmeyer flasks, glass connecting tubes, rubber tubing.
8. KEYWORD INDEX: Ultimate analysis; carbon, hydrogen, nitrogen, oxygen; absorption tube, Kjeldahl-Gunning.	
9. CROSS REFERENCE ID NUMBERS 01-03-01-02; 02-01-03-02.	
10. REFERENCES	
A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D271-70, "Standard Methods of Laboratory Sampling and Analysis of Coal and Coke," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 22-27. B) BACKGROUND INFORMATION 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D271-70, "Standard Methods of Laboratory Sampling and Analysis of Coal and Coke," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 14-16. C) FIELD APPLICATIONS 014 Hamersma, J.W., and S.L. Reynolds, "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," TRU Systems Group, EPA Contract No. 68-02-1412, March 1975.	

1. TITLE ANALYSIS OF COAL AND COKE ASH FOR ALUMINUM, SILICON, IRON, TITANIUM, PHOSPHOROUS, CALCIUM AND SODIUM BY PHOTOMETRY AND/OR CHELATOMETRIC TITRATION	2. IDENTIFICATION CODE 02-02-01-04
3. ABSTRACT OF METHODOLOGY The sample to be analyzed (see 01-03-01 and 02-04-03-02 for sample collection and preparation procedures) is ashed under standard conditions and ignited to constant weight. Two solutions are then prepared from the ash: Solution A, (for SiO_2 and Al_2O_3 analyses) by fusing the ash with sodium hydroxide followed by final dissolution of the melt in dilute hydrochloric acid; Solution B, (for the remaining elements), by decomposition of the ash with sulfuric, hydrofluoric and nitric acids. The two solutions are subsequently analyzed by a combination of methods: a) spectrophotometric procedures for SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and P_2O_5; b) chelatometric titration for CaO and MgO; and c) flame photometry for Na_2O and K_2O. Figure 02-02-01-04A summarizes the methods and procedures for each determination.	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE The methods are applicable to all solid samples (coal, coke, etc) which have been collected from process streams. Analyses are best performed by commercial analytical laboratories. B) INTERFERENCES/LIMITATIONS Insoluble barium sulfate may precipitate out in the sample diluted for chelatometric determination of calcium. However, the precipitate may be removed by filtration. C) RECOMMENDED USE AREA Engineering evaluation R&D.	
5. OPERATIONAL PARAMETERS A) RANGE Methods have ppm sensitivities. B) ACCURACY 5% or better. C) PRECISION $\pm 10\%$	
6. REAGENTS REQUIRED See Table 02-02-01-04A for summary of specific required reagents. Reagents for general analysis solutions include: hydrochloric acid, hydrofluoric acid, NBS No. 99a Soda Feldspar ($\text{SiO}_2 + \text{Al}_2\text{O}_3$), nitric acid, sodium hydroxide, and sulfuric acid.	7. EQUIPMENT REQUIRED Laboratory balance, crucibles, muffle furnace, emission flame photometer, absorption spectrophotometer (380 to 780 nm).
8. KEYWORD INDEX: Elemental analysis; coal ash; coke ash; silicon, aluminum, iron, titanium, phosphorous, calcium and sodium.	
9. CROSS REFERENCE ID NUMBERS 01-03-01-02; 02-04-03-02; see also 02-02-01-12 and 02-02-01-14.	
10. REFERENCES A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D2795-69, "Standard Methods of Analysis of Coal and Coke Ash," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 407-414. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, E200-67, "Standard Methods for Preparation, Standardization and Storage of Standard Solutions for Chemical Analysis," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 868-885. C) FIELD APPLICATIONS 203 Novitskii, N.V., and N.I. Ivanova, <u>Khim. Tverd. Topl.</u>, 4, 64-8, 1973 (Russ); <u>Chem. Abstr.</u>, 69, 5586.	

TITLE ANALYSIS OF COAL AND COKE ASH FOR ALUMINUM, SILICON, IRON, TITANIUM, PHOSPHOROUS, CALCIUM AND SODIUM BY PHOTOMETRY AND/OR CHELATOMETRIC TITRATION (CONTINUED)

ID NO. 02-02-01-04

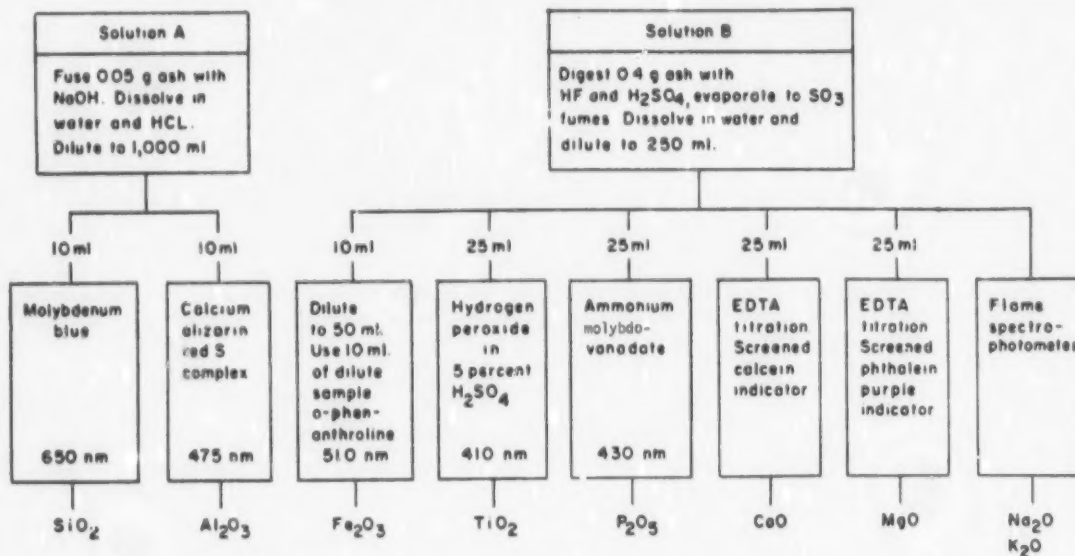


Figure 02-02-01-04A. Outline of Rapid Methods for Analysis of Coal Ash (Reference 057).

Table 02-02-01-04A. Summary of Reagents Required for Analysis.

Species	Reagents Required
SiO ₂	Ammonium molybdate solution, sodium sulfite, 1-amino-2-naphthol-4-sulfonic acid, sodium metabisulfite, tartaric acid solution.
Al ₂ O ₃	Glacial acetic acid, Alizarin Red-S solution, calcium chloride solution, sodium acetate-acetic acid buffer, hydroxylamine, hydrochloride solution, thioglycollic acid.
Fe ₂ O ₃	Hydroxylamine hydrochloride solution, orthophenanthroline, sodium citrate, ferrous ammonium sulfate.
TiO ₂	3% hydrogen peroxide, NBS Sample No. 154a (99.6% TiO ₂), potassium pyrosulfate, potassium bisulfate.
P ₂ O ₅	Ammonium molybdovanadate, potassium dihydrogen phosphate.
CaO	Ammonium hydroxide, calcein indicator (thymolphthalein and potassium chloride), EDTA, potassium hydroxide, calcium carbonate, triethanolamine.
MgO	Ammonium hydroxide, phthalein purple indicator (phthalein purple, methyl red, Naphthol Green 15, potassium chloride), triethanolamine, EDTA.
Na ₂ O, K ₂ O	Potassium sulfate solution; sodium sulfate solution, synthetic ash solution (aluminum, calcium carbonate, magnesium sulfate, sulfuric acid).

IDENTIFICATION CODE

1. TITLE ATOMIC ABSORPTION TECHNIQUES FOR Ba, Be, Cd, Ca, Cr, Cu, Pb, Mn, Hg, Ni, V, Zn
Al, Sb, Ag, Co, Fe, Mg, Mo, K, Ag, Na, Th, Sn, Ti

02-02-01-05

3. ABSTRACT OF METHODOLOGY

AAS (atomic absorption spectrometry) as a general analytical tool is normally considered free of interelement interferences, and, because of the large dilutions employed, is usually unresponsive to matrix changes. High solids concentrations after typical dissolution procedures as well as complicated matrices make it mandatory for the analyst to be aware of and to investigate the presence of interferences. The interference types encountered are classified into the following three categories:

- Interelement or chemical interferences. For the most part, these interferences when present can be eliminated by using a high temperature H_2O -acetylene flame, or by adding suppressants.
- Matrix effects. These effects are compensated for by specially preparing the standards to match the expected acid and salt content of the sample, or by applying standard addition techniques.
- Molecular absorptions. Molecular absorptions occur from species such as $CaOH$ or SrO or from organic materials. The end result is a positive error in the absorption measurement. A double beam AAS is required to both monitor this molecular absorption and apply the appropriate correction electronically.

The solutions prepared as described in 02-01-02, 03, 04 can be analyzed directly by AAS for Mn, Cu, Cr, Ni, Sn, V, Pb, Cd, Zn, Ba, Cd, Ca, and Be using the operating conditions specified in Table 02-02-01-05A. If no chemical or matrix interferences are found after performing accuracy checks, it is possible to use distilled water standards. The implementation of either the factor method short curve or standard addition technique for obtaining the required accuracy is sample dependent and also depends on the skill of the analyst.

4. APPLICATION: Engineering evaluation R&D, compliance**A) OPERATIONAL SCOPE**

These procedures can be used on all samples generated from 02-01-02, 03, 04.

B) INTERFERENCES/LIMITATIONS

It is possible that matrix problems will reduce the sensitivities reported in Table 02-02-01-05A

C) RECOMMENDED USE AREA

These methods are especially useful for engineering evaluation R&D but at the same time they are the recommended compliance procedures.

5. OPERATIONAL PARAMETERS

A) RANGE See Table 02-02-01-05A.

B) ACCURACY $\pm 15\%$

C) PRECISION $\pm 10\%$

6. REAGENTS REQUIRED

None

7. EQUIPMENT REQUIRED

Double beam AAS (Jarrel-Ash 810 or equivalent).

8. KEYWORD INDEX: Analysis, atomic absorption spectrometry.**9. CROSS REFERENCE ID NUMBERS** 02-01-02, 03, 04; 02-01-01-02.**10. REFERENCES****A) PRIMARY SOURCE**

0185 "Methods for Chemical Analysis of Water and Wastes", "Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, D.C., 1974.

B) BACKGROUND INFORMATION

See Table 02-02-01-05A.

C) FIELD APPLICATIONS

See Table 02-02-01-05A.

ID NO. 02-02-01-05

TITLE ATOMIC ABSORPTION TECHNIQUES FOR Ba, Be, Ca, Cr, Cu, Pb, Mn, Hg, Ni, V, Zn
Al, Sb, Ag, Co, Fe, Mg, Mo, K, Mo, Ag, Na, Th, Sn, Ti (CONTINUED)

Table 02-02-01-05A. Typical Atomic Absorption Operating Parameters

Element	Slit Width (mm)	Wavelengths, nm		Gas Mixture	Detection Limit (ppm)	Comments	References
		Analytical	Background				
Ba	0.4	553.6	-	N ₂ O acetylene	0.03	Add 0.1%K as an ionization suppressant	084, 205, 209, 185
Be	1.0	234.9	Ni-231.6 Non-Absorbing	N ₂ O acetylene	0.005		084, 205, 209, 218, 185
Cd	0.4	228.8	226.5	Air acetylene	0.003		084, 024, 205, 207, 209, 210, 213, 216, 185
Ca	1.0	422.7	-	N ₂ O acetylene	0.005	Add 1%K as an ionization suppressant	084, 024, 205, 207, 209, 210, 213, 216, 185
Cr	0.2	357.9	351.9	N ₂ O acetylene	0.005		084, 024, 205, 207, 213, 185
Cu	1.0	324.7	323.4	Air acetylene	0.003		084, 204, 205, 209, 210, 213, 216, 217, 185
Pb	0.4	283.3	282.0	Air acetylene	0.03		084, 024, 205, 209, 213, 216, 217, 185
Mn	0.4	279.5	Pb 282.0 Non-Absorbing	Air acetylene	0.003		084, 204, 024, 209, 211, 213, 216, 217, 185
Hg	1.0	253.7	Si 252.5	Flameless	0.1 µg	Reduction using SnCl ₂	205, 206, 209, 212, 219
Ni	0.2	232.0	231.6	Air acetylene	0.01		024, 205, 209, 213, 217
V	1.0	318.4	312.5	N ₂ O acetylene	0.01		205, 208, 209, 214
Zn	1.0	318.4	210.0	Air acetylene	0.003		084, 204, 024, 205, 209, 210, 213, 216, 217
Al	N/A	309.2	-	N ₂ O acetylene	0.1 mg/l	Add 1,000 µg/ml as ionization suppressant	204, 185
Sb	N/A	217.6	-	Air acetylene	0.2 mg/l	Interference due to Pb may occur; use 231.1 line	185
As	N/A	193.7	-	Argon hydrogen	2-20 µg/l		185
Co	N/A	240.7	-	Air acetylene	0.03 mg/l		185
Fe	N/A	248.3	-	Air acetylene	0.02 mg/l		185
Mg	N/A	285.2	-	Air acetylene	0.0005 mg/l	Interference due to Al at conc greater than 2 mg/l is masked by addition of lanthanum	185
Mn	N/A	279.5	-	Air acetylene	0.01 mg/l		185
Mo	N/A	313.3	-	N ₂ O acetylene	0.1 mg/l		185
K	N/A	766.5	-	Air acetylene	0.005 mg/l	Sodium may interfere if present at levels significantly higher than potassium	185
Ag	N/A	328.1	-	Air acetylene	0.01 mg/l		185
Na	N/A	589.6	-	Air acetylene	0.002 mg/l		185
Th	N/A	276.8	-	Air acetylene	0.1 mg/l		185
Sn	N/A	286.3	-	Air acetylene	0.8 mg/l		185
Ti	N/A	365.3	-	N ₂ O acetylene	0.3 mg/l		185

TITLE ATOMIC ABSORPTION TECHNIQUES FOR Ba, Be, Ca, Cr, Cu, Pb, Mn, Hg, Ni, V, Zn
Al, As, Ag, Co, Fe, Mg, Mn, Mo, K, Ag, Na, Th, Sn, Ti (CONTINUED)

ID NO. 02-02-01-06

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- 209 Slavin, W., "Atomic Absorption Spectrometry," Wiley Interscience Publishers, New York, N.Y., 1968, 307 pp.
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1. TITLE DETERMINATION OF ACIDITY BY ELECTROMETRIC TITRATION		2. IDENTIFICATION CODE 02-02-01-06
3. ABSTRACT OF METHODOLOGY		
The method involves the determination of total acidity, due to strong and weak acids, plus acidity resulting from the formation of stable hydroxy complexes by metal ions. The initial pH of the sample is measured with a pH meter. If the pH is above 4.0, standard sulfuric acid is added to lower pH to 4 or less. Hydrogen peroxide is then added for the oxidation and hydrolysis of polyvalent cations, such as iron and aluminum salts. After boiling and cooling to room temperature, the sample is titrated electrometrically with standard alkali to pH 8.2. Acidity is then reported as equivalent concentration of hydrogen ions in milligrams per liter, or alternatively, as equivalents of calcium carbonate.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous streams (liquid and slurry discharges) including surface waters, sewages, and other industrial wastes. B) INTERFERENCES/LIMITATIONS A sluggish electrode response may be observed due to presence of suspended matter or precipitates formed during the titration. This is offset by slow, dropwise addition of titrant near the endpoint, or by 15-20 second pauses between titrant additions. C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment procedure for the measurement of mineral acidity of aqueous effluents, plus acidity from oxidation and/or hydrolysis of polyvalent cations (iron and aluminum salts) and is applicable to all liquid/slurry streams.		
5. OPERATIONAL PARAMETERS		
A) RANGE 10 to 1,000 mg/liter acidity as CaCO_3, using samples having volumes of 50 ml. B) ACCURACY 10% relative error or less. C) PRECISION ± 10 mg/liter.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Hydrogen peroxide, 0.02N standard sodium hydroxide, 0.02N standard sulfuric acid, indicators (Bromocresol Green, Methyl Orange, Methyl Purple, Methyl Red, Phenolphthalein).		Pipet, Erlenmeyer flask, electrometric titration apparatus.
8. KEYWORD INDEX: Acidity, aqueous effluents, liquid/slurry, electrometric titration.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-02, 01-02-02-01.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, Natl. Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 1-2. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, ASTM Method D-1067, "Standard Methods of Test for Acidity or Alkalinity of Water," American Society for Testing and Materials, Philadelphia, PA., 1971, Method B, p. 138. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, ASTM D1293-65, "Standard Method of Test for pH of Industrial Water and Industrial Wastewater," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 240-248. 084 American Public Health Association (APHA), American Water Works Association and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 201, p. 370. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF ARSENIC BY SILVER DIETHYL DITHIOCARBAMATE METHOD		2. IDENTIFICATION CODE 02-02-01-07
3. ABSTRACT OF METHODOLOGY		
Inorganic arsenic compounds are reduced to arsine by zinc in an acid medium. The resulting gas mixture is passed through a scrubber packed with glass wool which has been impregnated with a lead acetate solution, and into an absorbing tube for subsequent digestion in a pyridine (or 1-ephedrine in chloroform) solution of silver diethyl dithiocarbamate. The red complex formed is measured spectrophotometrically at 535 nm, and arsenic is determined by reference to an analytical curve prepared from standards.		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous streams (liquids and slurries) including surface, ground and saline water, domestic and industrial effluents. B) INTERFERENCES/LIMITATIONS High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver may provide interference. Industrial effluents having high concentrations of organic matter may be oxidized prior to digestion (see Ref. 204). C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D procedure for the determination of total inorganic arsenic. Industrial wastes having low arsenic concentrations may be concentrated prior to digestion, or spiked with a known concentration of arsenic in order to improve accuracy. Streams having high trace metal concentrations may provide interference.		
5. OPERATIONAL PARAMETERS		
A) RANGE Inorganic arsenic is determined at concentrations of 10 µg/liter or greater. B) ACCURACY Relative error of 0% has been achieved in analyses performed on synthetic unknown samples having 40 µg/liter arsenic. C) PRECISION Relative standard deviation of 13.8% has been achieved in analyses performed on synthetic unknown samples having 40 µg/liter arsenic.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Lead acetate; silver diethyl dithiocarbamate solution in pyridine (or 1-ephedrine in chloroform).	Beakers; spectrophotometer; arsine generator, scrubber and absorber, glass wool.	
8. KEYWORD INDEX: Arsenic, aqueous effluents, silver diethyl dithiocarbamate method, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center EPA No. 625/6-74-003, Washington, 1974, p. 9-10. B) BACKGROUND INFORMATION 204 American Public Health Association (APHA), American Water Works Association and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 104(A), p. 62. 204 American Public Health Association (APHA), American Water Works Association and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 104(B), Procedure 4a, p. 65. C) FIELD APPLICATIONS 205 Liederman, D., J.E. Downen and D.I. Milner, "Determination of Arsenic in Petroleum Stocks and Catalysts by Evolution of Arsine," <i>Anal. Chem.</i>, 31, 2052 (1959). 206 Miller, J.T., and H.G. Byers, "Selenium Spring," <i>Ind. Eng. Chem., News Ed.</i>, 13, 456 (1935). 207 Stratton, G., and H.C. Whitehead, "Colorimetric Determination of Arsenic in Water with Silver Diethyl Dithiocarbamate," <i>Amer. Water Works Assoc., J.</i>, p. 54, 861 (1962). 208 U.S. Public Health Service, "Drinking Water Standards," Public Health Service Pub., 956, p. 7 (1962).		

1. TITLE DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND USING BIOASSAY PROCEDURES	2. IDENTIFICATION CODE 02-02-01-08
3. ABSTRACT OF METHODOLOGY Method involves use of empirical bioassay-type procedure to measure the dissolved oxygen consumed by microbial life in the digestion of organic matter present in a sample. A sample is incubated in the dark at 20°C for 5 days. Dissolved oxygen is measured both before and after incubation using either the Modified Winkler with Full Bottle Technique (see 02-02-01-09) or the probe method (02-02-01-10).	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to all aqueous streams (liquids and slurries) including industrial effluents. B) INTERFERENCES/LIMITATIONS None C) RECOMMENDED USE AREA This is the recommended compliance method for BOD for all aqueous effluents.	
5. OPERATIONAL PARAMETERS	
A) RANGE N/Q; typical BOD range from one to several hundred mg/liter. B) ACCURACY No acceptable procedure exists for measurement of accuracy of BOD test. C) PRECISION Standard deviations of ± 0.7 and ± 26 mg/liter BOD were observed for mean values of 2.1 and 175 mg/liter BOD.	
6. REAGENTS REQUIRED See 02-02-01-09 and 02-02-01-10.	7. EQUIPMENT REQUIRED Incubator
8. KEYWORD INDEX: Biochemical oxygen demand (BOD), aqueous effluents, oxygen requirements.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-02, 01-02-02-01; 02-02-01-09, 02-02-01-10.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 11-12. B) BACKGROUND INFORMATION 204 American Public Health Association (APHA), American Water Works Association and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 219, p. 489. C) FIELD APPLICATIONS	

1. TITLE DETERMINATION OF DISSOLVED OXYGEN (MODIFIED WINKLER WITH FULL-BOTTLE TECHNIQUE)		2. IDENTIFICATION CODE 02-02-01-09
3. ABSTRACT OF METHODOLOGY		
Method involves treatment of sample with manganous sulfate, a solution of potassium hydroxide, potassium iodide (and sodium azide, optional) and sulfuric acid. The manganous hydroxide precipitate combines with the dissolved oxygen to form a new brown precipitate of manganic hydroxide, which is converted to manganic sulfate upon acidification. The manganic sulfate reduces the potassium iodide and releases free iodine, which is then titrated with sodium thiosulfate or phenylarsine oxide (PAO) using starch as the indicator.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to liquid/slurry effluents (drinking, surface and saline waters, domestic and industrial wastes) containing not more than one mg/liter of ferric iron (up to 200 mg/liter, if 1 ml of fluoride solution is added before sample modification). B) INTERFERENCES/LIMITATIONS Other interferences include nitrite nitrogen (eliminated by the Alsterberg azide modification) and high organic content (compensated for by the Trerault procedure). Samples containing sulfite, thiosulfate, polythionate, chlorine or hypochlorite, high suspended solids, organics which are oxidized by alkali and iodine, untreated domestic sewage, biological flocs, and highly colored samples interfere with the azide modification. C) RECOMMENDED USE AREA This is the recommended compliance procedure for the determination of DO in aqueous effluents not high in organic content (ash dewatering effluent, product gas dehydration units, etc.).		
5. OPERATIONAL PARAMETERS		
A) RANGE N/Q B) ACCURACY 10% relative error or less. C) PRECISION Reproducibility of 0.2 ppm DO at the 7.5 ppm level has been reported.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Manganous sulfate; potassium hydroxide; potassium iodide; conc. sulfuric acid; sodium thiosulfate, (sodium and potassium azide-optional, starch suspension).		BOD sample bottle; laboratory glassware; titration assembly.
8. KEYWORD INDEX: Dissolved oxygen (DO), aqueous effluents, Modified Winkler.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-08.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974. p. 51-55. B) BACKGROUND INFORMATION 209 Kroner, R.C., R. Gorman and J. Longbottom, "A Comparison of Various Reagents Proposed for Use in the Winkler Procedure for Dissolved Oxygen," PHS Water Pollution Surveillance System Applications and Development, Report No. 12, Water Quality Section, Basic Data Branch, July 1964. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF DISSOLVED OXYGEN (DO) BY ELECTRODE (PROBE) METHOD		2. IDENTIFICATION CODE 02-02-01-10
3. ABSTRACT OF METHODOLOGY		
The electrode (probe) method uses commercially available probes for the determination of dissolved oxygen (DO). These include membrane probes and thallium probes. Membrane probes measure partial pressure of oxygen, which is a function of dissolved organic salts; the current or potential is then correlated with DO concentrations. The thallium probe requires salt concentrations which provide a minimum conductivity of 200 micromhos.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid and slurry) streams, including those excluded from the Modified Winkler procedure (see 02-02-01-09). B) INTERFERENCES/LIMITATIONS When membrane probes are used, reactive gases (chlorine, hydrogen sulfide) may interfere. For thallium probes, sulfur compounds such as hydrogen sulfide, sulfur dioxide and mercaptans, may cause interference. Dissolved organics do not cause interference. Membrane performance is not affected by pH changes. C) RECOMMENDED USE AREA This is the recommended compliance procedure for DO determination for all aqueous streams (ash dewatering effluent, condensate recycle water, product dehydration effluent) which are low in sulfur compounds.		
5. OPERATIONAL PARAMETERS		
A) RANGE Standard probes have sensitivity of 0.05 mg/liter. B) ACCURACY $\pm 1\%$ accuracy. C) PRECISION 0.1 mg/liter repeatability.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
N/A		Probe, such as: Weston and Stack DO Analyzer Model 30; Yellow Springs Instrument (YSI) Model 54; Beckman Fieldlab Oxygen Analyzer.
8. KEYWORD INDEX: Dissolved oxygen (DO), aqueous effluent, probe method.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02; 02-02-01-08, 02-02-01-09.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 56-58. B) BACKGROUND INFORMATION 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 51-55. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF BORON BY CURCUMIN METHOD		2. IDENTIFICATION CODE 02-02-01-11
3. ABSTRACT OF METHODOLOGY		
Method involves sample acidification and evaporation in the presence of curcumin to form the red-colored rosocyanine. The rosocyanine is then extracted into a suitable solvent (ether, alcohol) and determined spectrophotometrically at 530 nm.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid and slurry streams) having 0.1-1.0 mg/liter boron (optimum range). B) INTERFERENCES/LIMITATIONS Interferences are nitrate nitrogen concentrations above 20 mg/liter, and total calcium and magnesium hardness above 100 mg/liter as CaCO₃. This is eliminated by use of a cation exchange resin. C) RECOMMENDED USE AREA This is an alternate compliance procedure for the determination of boron in most industrial aqueous effluents, (i.e., ash dewatering effluent, condensate recycle water, dehydration and cooling water, etc.) (see 02-02-01-05).		
5. OPERATIONAL PARAMETERS		
A) RANGE 1 mg/liter or below. B) ACCURACY 0% relative error on the synthetic sample determinations described below (5c). C) PRECISION Relative standard deviation of 22.8% measured on synthetic samples prepared by Analytical Reference Service, PHS, containing 240 µg/liter Be, 20 µg/liter Se, and 6 µg/liter V, in 30 laboratories.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Concentrated standard acid, curcumin.	Standard laboratory glassware; spectrophotometer.	
8. KEYWORD INDEX: Boron, aqueous effluents, curcumin method, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02-02, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 13. B) BACKGROUND INFORMATION 204 American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 107A, p. 69. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF CALCIUM BY TITRIMETRY		2. IDENTIFICATION CODE 02-02-01-12
3. ABSTRACT OF METHODOLOGY		
Method involves titration of calcium with EDTA (disodium dihydrogen ethylenediamine tetraacetate). EDTA forms a colorless stable complex with calcium. The murexide indicator is dark purple in the absence of calcium, but forms a light salmon-colored complex with calcium. The endpoint of the titration is determined visually.		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid/slurry) streams containing dissolved calcium, including domestic and industrial effluents and drinking and surface waters. B) INTERFERENCES/LIMITATIONS Strontium and barium interfere; alkalinity of 30 mg/liter interferes. Magnesium interference is eliminated by raising pH between 12-13 to precipitate magnesium hydroxide. The heavy metal interferences can be eliminated using alkaline hydroxide and sulfide treatments. C) RECOMMENDED USE AREA This is an alternative compliance procedure for the determination of calcium in most aqueous effluents with low alkalinity (see 02-02-01-05).		
5. OPERATIONAL PARAMETERS		
A) RANGE Lower detection limit is 0.5 mg/liter as CaCO₃; the upper detection limit can be extended to all concentrations by sample dilution, to 25 mg as CaCO₃, or less. B) ACCURACY 1.9% in 44 laboratories using synthetic unknown samples containing 108 mg/liter Ca, 83 mg/liter Mg, 3.1 mg/liter K, 19.9 mg/liter Na, 241 mg/liter chloride, 1.1 mg/liter nitrate, 250 µg liter/nitrite nitrogen, 259 mg/liter sulfate and 42.5 mg/liter (total alkalinity). C) PRECISION Relative standard deviation of 9.2% on samples described above.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
EDTA, murexide indicator, standard base for pH adjustment (optional).	Standard laboratory glassware; visual titration assembly.	
8. KEYWORD INDEX: Calcium, aqueous effluents, titrimetric method.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 19. B) BACKGROUND INFORMATION 204 American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 110C, p. 84. 210 Banks, J., "The Volumetric Determination of Calcium and Magnesium by the Ethylenediamine Tetraacetate Method," <i>Analyst</i>, <u>77</u>, 484 (1952). C) FIELD APPLICATIONS 211 Brown, E., et al., "Methods for Collection and Analyses of Water Samples for Dissolved Minerals and Gases," Chapter A-1 of "Techniques of Water-Resources Investigations of the United States Geological Survey," Washington, 1970, p. 64-67. 210 Banks, J., "The Volumetric Determination of Calcium and Magnesium by the Ethylenediamine Tetraacetate Method," <i>Analyst</i>, <u>77</u>, 484 (1952).		

1. TITLE DETERMINATION OF TOTAL RESIDUAL CHLORINE BY AMPEROMETRIC TITRATION OR IODOMETRIC TITRATION	2. IDENTIFICATION CODE 02-02-01-13
3. ABSTRACT OF METHODOLOGY Method involves titration of a buffered sample contained in an amperometric titration cell with phenyl arsine oxide (PAO). Endpoint is reached when the generation of current ceases (working electrode vs sat. Ag/AgCl set at +1.13 v). When chlorine is present as the chloramine, potassium iodide is added and an iodometric titration is performed. The chlorine liberates free iodine from potassium iodide solutions when the pH is 8 or below. The liberated iodine is then titrated with a standard solution of sodium thiosulfate or phenylarsine oxide (PAO) with starch as an indicator.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to all aqueous streams (liquids and slurries) which do not contain large quantities of organic matter.	
B) INTERFERENCES/LIMITATIONS Organic material interference; color, turbidity, iron, manganese and nitrate nitrogen do not interfere.	
C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of total residual chlorine for aqueous streams low in organic matter (i.e., ash dewatering effluents, cooling tower waters, etc.).	
5. OPERATIONAL PARAMETERS	
A) RANGE Method is applicable to samples containing 5 mg/liter or below.	
B) ACCURACY N/Q	
C) PRECISION N/Q	
6. REAGENTS REQUIRED Phenylarsine oxide; buffer solution; potassium iodide; sodium thiosulfate; starch.	7. EQUIPMENT REQUIRED Amperometric titration cell, or standard manual titration assembly.
8. KEYWORD INDEX: Chlorine, total residual; aqueous effluents; amperometric titration; iodometric titration.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 35.	
B) BACKGROUND INFORMATION 204 American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, Method 204A, p. 382. 024 "STM Committees D-19 and D-22, "Water; Atmospheric Analysis," Part 23, Method D1253-68 (1973), "Standard Methods of Test for Residual Chlorine in Industrial Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 214.	
C) FIELD APPLICATIONS 212 California State Water Quality Control Board, "Water Quality Criteria," Pub. 3-A, p. 162 (1963).	

1. TITLE DETERMINATION OF SILICA (DISSOLVED)		2. IDENTIFICATION CODE 02-02-01-14
3. ABSTRACT OF METHODOLOGY		
Method involves filtration of sample through a membrane filter, followed by addition of molybdate ion in acidic solution to the filtrate. The resultant greenish-yellow silico-molybdate complex is then measured spectrophotometrically at 700 nm. The silico-molybdate complex may form as alpha and beta polymorphs, which have absorbance maxima at different wavelengths. The addition of acid (to pH 2.5) favors the development of the preferred beta form.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid and slurry) streams, including drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Excessive color and turbidity interfere but may be corrected by blank determinations using uncomplexed sample. Phosphate interferes, but is suppressed by addition of tartaric acid. Hydrogen sulfide may be removed by boiling. Addition of EDTA prevents interference by high iron concentrations, and also complexes calcium. C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of dissolved silica in aqueous effluents.		
5. OPERATIONAL PARAMETERS		
A) RANGE 2 to 25 mg silica/liter. The upper range may be extended by taking sample aliquots; the lower range, by treatment of the sample with amino-naphthol-sulfonic acid, with subsequent spectrophotometric measurement. B) ACCURACY N/Q C) PRECISION 4% of the quantity of silica measured, using samples with 2 to 50 mg/liter. Precisions of ± 0.10 mg/liter are obtained in the range from 0 to 2 mg/liter.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Ammonium molybdate solution; amino-naphthol-sulfonic acid (optional); hydrochloric acid; standard silica solution, EDTA; tartaric acid.	Spectrophotometer; 0.45 μ membrane filter, standard laboratory glassware.	
B. KEYWORD INDEX: Silica, dissolved; aqueous effluents; spectrophotometry; ammonium molybdate.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 274. 213 Brown, E., "Techniques of Water-Resources Investigations of the U.S. Geological Survey," Washington, 1970, p. 139. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-23, "Water; Atmospheric Analysis," Part 23, D859-68, "Standard Methods of Test for Silica in Industrial Water and Industrial Waste Water," American Society for Testing and Materials, Philadelphia, PA., 1973, p. 401. 204 Standard Methods for the Examination of Water and Wastewater, 13th ed., Method 151B, 1971, p. 303. 214 Strickland, J.D.H., "The Preparation and Properties of Silicomolybdic Acid; I. The Properties of Alpha Silicomolybdic Acid," JACS, 74, 862 (1952). 215 Govett, G.J.S., "Critical Factors in the Colorimetric Determination of Silica," Anal. Chem. Acta, 25, 69 (1961). C) FIELD APPLICATIONS 216 Minhoff, C.E., "Boiler Water Conditioning to Prevent Turbine Deposits," Petroleum Refiner, 27, 438 (1948).		

1. TITLE SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY		2. IDENTIFICATION CODE 02-02-01-15
3. ABSTRACT OF METHODOLOGY		
In preparation for spectrophotometric determination, the sample is digested using $H_2SO_4 - HNO_3$. Oxidizing conditions must be maintained. The digest or aliquot is then transferred to a 125 ml Erlenmeyer. Sulfuric acid is added to make a total of 5 ml of the acid, and the sample is evaporated to fumes of SO_3. The flask is cooled, perchloric acid is added and the digest is again evaporated to white fumes. The digest is cooled in an ice bath 30 minutes, and 5 ml precooled 3N H_3PO_4 is added. Then 5 ml of precooled Rhodamine B solution is added, and the flask is stoppered and shaken vigorously. The sample is transferred to a precooled 125 ml separator. Next, 10 ml of precooled benzene are pipetted into the separator, which is then shaken vigorously. The benzene layer (red if Sb is present) is then transferred to a test tube in order to let the water settle. The sample is then measured spectrophotometrically at 565 nm against a benzene blank. Concentration of Sb is determined by comparison to a standard curve.		
4. APPLICATION: Environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) effluents, including surface and saline water, domestic and industrial effluents. B) INTERFERENCES/LIMITATIONS The individual operations in the procedure should be performed as quickly as possible, particularly up until the color is extracted into benzene. The color is stable in benzene for several hours. C) RECOMMENDED USE AREA This is an alternative engineering R&D procedure for the determination of antimony in aqueous effluents where the AAS procedure is inoperable.		
5. OPERATIONAL PARAMETERS		
A) RANGE All concentrations of antimony can be determined, using suitable aliquots. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Hydrochloric acid, dilute phosphoric acid, Rhodamine B solution, antimony standard solutions, sulfuric acid, benzene.	Spectrophotometer; standard laboratory glassware, including stoppered Erlenmeyer flasks.	
8. KEYWORD INDEX: Antimony, aqueous effluents, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, July 1975. B) BACKGROUND INFORMATION 173 ASTM Committee E-2, E-3 and E-16, "Chemical Analysis of Metals; Sampling and Analysis of Metal-Bearing Ores," 1971 Annual Book of ASTM Standards, Part 32 E87, "Photometric Methods for Chemical Analysis of Lead, Tin, Antimony and Their Alloys," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 463. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF SELENIUM BY DIAMINO BENZIDINE METHOD	2. IDENTIFICATION CODE 02-02-01-16
3. ABSTRACT OF METHODOLOGY	
Method involves oxidation of all selenium compounds found in the sample to selenate using potassium permanganate. The selenate is then reduced to selenite in warm dilute hydrochloric acid. Diaminobenzidine is then added, and the resultant species (piaselenol) is determined spectrophotometrically at 420 nm.	
4. APPLICATION: Environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including natural waters and industrial effluents, not containing high concentrations of iodide and bromide. B) INTERFERENCES/LIMITATIONS Iodide and bromide interfere. Compounds which oxidize the diaminobenzidine reagent interfere, although EDTA removes this interference. C) RECOMMENDED USE AREA This is the recommended environmental assessment method for the determination of selenium in aqueous samples.	
5. OPERATIONAL PARAMETERS	
A) RANGE Method is applicable to all ranges of selenium, using suitable aliquots. B) ACCURACY N/Q C) PRECISION Analysis of 3 test samples by 7 laboratories resulted in means of 49, 84 and 10ug/liter, with standard deviations of 6, 8 and 5ug/liter, respectively.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Ammonium chloride, ammonium hydroxide, calcium chloride, diaminobenzidine solution, EDTA-sulfate reagent, hydrochloric acid, methyl orange indicator (optional), standard selenium solutions.	Spectrophotometer for use at 420 nm; standard laboratory glassware; standard titration assembly (optional, for interference removal).
8. KEYWORD INDEX: Selenium, aqueous effluents, diaminobenzidine method, spectrophotometry.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 217 "Techniques of Water-Resources Investigations of the U.S. Geological Survey," Chapter A1, "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," Washington, 1970, p. 135-7. B) BACKGROUND INFORMATION 218 California State Water Quality Control Board, "Water Quality Criteria," Pub. 3-A, p. 253 (1963). 219 Rossum, J.R., and P.A. Villarruz, "Suggested Methods for Determining Selenium in Water," <u>Am. Water Works Assoc. Jour.</u>, V. 54, p. 746 (1962). C) FIELD APPLICATIONS 220 Scott, R.C., and P.T. Voegeli, "Radiochemical Analyses of Ground and Surface Water in Colorado, 1954-1961," Colorado Water Conserv. Board Basic-Data Rept. 7, 1961. 221 Maag, D.D., and M.W. Gleen, "Toxicity of Selenium: Farm Animals," Sec. III in "Selenium in Biomedicine-A Symposium," The Avi Publishing Co., Westport, Conn., p. 127-140, 1967. 222 Muth, O.H. (ed.), "Selenium in Biomedicine," The Avi Publishing Co., Westport, Conn., p. 445, 1967.	

1. TITLE DETERMINATION OF SELENIUM BY DISTILLATION -- DIAMINO BENZIDINE METHOD		2. IDENTIFICATION CODE 02-02-01-17
3. ABSTRACT OF METHODOLOGY		
Sample is treated with bromine to form the volatile tetrabromide. The tetrabromide is distilled, along with a minimum of excess bromine, and condensed and absorbed into a beaker of water. The excess bromine is removed by precipitation with a phenol solution as tribromophenol, and the tetravalent selenium is subsequently treated with diaminobenzidine (see 02-02-01-16) and determined spectrophotometrically at 420 nm.		
4. APPLICATION: Environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including natural waters and industrial effluents, and including waters containing high concentrations of iodide and bromide. B) INTERFERENCES/LIMITATIONS No known interferences. C) RECOMMENDED USE AREA This is the alternate recommended environmental assessment method for the determination of selenium, particularly for samples containing bromide and iodide. (see 02-02-01-16)		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is applicable to all ranges of selenium, using suitable aliquots. B) ACCURACY N/Q C) PRECISION No precision data are available; see 02-02-01-16 for results of diaminobenzidine method.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Calcium chloride, diaminobenzidine solution, hydrochloric acid, methyl orange indicator, potassium permanganate, standard selenium solutions, sodium hydroxide, ammonium hydroxide, hydrogen peroxide, phenol solution; potassium bromide-acid reagent.	Distillation assembly; standard laboratory glassware, standard titration assembly (optional, for interference removal), spectrophotometer for use at 420 nm.	
8. KEYWORD INDEX: Selenium, aqueous effluents, distillation-diaminobenzidine method, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02; 02-02-01-16.		
10. REFERENCES		
A) PRIMARY SOURCE 217 Techniques of Water Resources Investigations of the U.S. Geological Survey, Chapter A1, "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," Washington, 1970, p. 137-9. B) BACKGROUND INFORMATION 218 California State Water Quality Control Board, "Water Quality Criteria," Pub. 3-A, p. 253 (1963). 222 Muth, O.H., ed., "Selenium in Biomedicine," Westport, Conn., The Avi Publishing Co., 1967, p. 445. 219 Rossum, J.R., and P.A. Villarruz, "Suggested Methods for Determining Selenium in Water," <i>Am. Water Works Assoc. Jour.</i>, 54, p. 746, 1962. C) FIELD APPLICATIONS 220 Scott, R.C., and P.T. Voegeli, "Radiochemical Analyses of Ground and Surface Water in Colorado, 1954-1961," Colorado Water Conserv. Board-Basic Data Rept. 7, 1961. 221 Maag, D.D., and M.W. Glenn, "Toxicity of Selenium: Farm Animals," Sec. III in "Selenium in Biomedicine-A Symposium," Westport, Conn., The Avi Publishing Co., p. 127-140.		

2. IDENTIFICATION CODE	
1. TITLE DETERMINATION OF CATIONS USING SPECIFIC ION ELECTRODES (SIE)	02-02-01-1B
3. ABSTRACT OF METHODOLOGY	
Specific ion electrodes can be used to determine the cations and species shown in Table 02-02-01-1BA. Samples can be determined by direct reading measurements, in which the electrode is inserted into the sample and a reading is taken, or by electrode titrations. There are 3 basic types of electrode titrations: R, S, and T. In R titrations, the electrode senses the reagent (R) species (usually an indicator) that is added to the sample prior to titration. In S titrations, the electrode senses the sample (S) species. In T titrations, the electrode senses the level of titrant (T) during the course of addition to the sample. The titration method allows determination of a number of species not directly sensed by the electrode; e.g., aluminum can be titrated with fluoride, using the fluoride electrode in a T type titration. R titrations can be used to measure nickel, zinc, manganese and strontium. Other applications are shown in Table 02-02-01-1BA.	
4. APPLICATION: Environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to samples (aqueous samples, species absorbed in liquids) containing cations and species shown in Table 02-02-01-1BA. B) INTERFERENCES/LIMITATIONS Extremes of pH may interfere. Anions which complex with specific cations may interfere in the analysis of the cation. C) RECOMMENDED USE AREA This is the applicable to level 1 environmental assessment procedure for determination of cations having concentration ranges listed in Table 02-02-01-1BA.	
5. OPERATIONAL PARAMETERS	
A) RANGE See Table 02-02-01-1BA for detectable concentrations of specific cations and species. Electrodes are capable of measuring ion activities well below concentration limits for cadmium, lead, cupric ion, and other cations. B) ACCURACY N/A C) PRECISION ± 0.1 or less in many cases.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Suitable precipitation or complexing agents, when required for specific analyses; e.g., EDTA for analysis of copper; pH adjusters and titrants (Table 02-02-01-01B).	Specific ion electrodes, specific ion meter or standard pH meter having an expanded millivolt scale standard laboratory glassware (beakers, pipettes, volumetric flasks).
8. KEYWORD INDEX: Specific ion electrodes, aqueous effluents, aqueous absorbed samples, cations.	
9. CROSS REFERENCE ID NUMBERS 02-03-02-01; 01-02-01-02, 01-02-02-01, 01-02-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 223 Orion Research, "Analytical Methods Guide," Orion Research, Inc., 7th ed., May 1975. B) BACKGROUND INFORMATION (See reverse side) C) FIELD APPLICATIONS (See reverse side)	

TITLE DETERMINATION OF CATIONS USING SPECIFIC ION ELECTRODES (SIE) (CONTINUED)

ID NO. 02-02-01-18

Table 02-02-01-18A. Cation and Species Analysis Using SIE (Reference 223).

Electrode	Type	Concentration Range (M)	Temperature Range (°C)	Interferences	Notes
• ammonia (ammonium)	gas sensing	10^0 to 10^{-6}	0-50	volatile amines	measures organic N after Kjeldahl digestion NO_3^- after reduction to NH_3
• cadmium	solid-state	10^0 to 10^{-7}	0-80	max level: Ag^+ , Hg^{++} , $\text{Cu}^{++} < 10^{-7}$ M; high levels of lead and ferric ion interfere	can be used for chelometric indicator titrations for metal ions, e.g., Zn^{++} , Ni^{++}
• calcium	liquid	10^0 to 10^{-5}	0-50	max level * (M) at 10^{-3} M Ca^{++} $\begin{cases} 0.3 \text{ Na}^+; 2 \times 10^{-6} \text{ Zn}^{++}; \\ 5 \times 10^{-6} \text{ Pb}^{++}; \\ 7 \times 10^{-5} \text{ Fe}^{++}, \text{Cu}^{++}; \\ 8 \times 10^{-3} \text{ Sr}^{++}, \text{Mg}^{++}; \\ 3 \times 10^{-2} \text{ Ba}^{++}; \\ 5 \times 10^{-2} \text{ Ni}^{++} \end{cases}$	
• carbon dioxide	gas sensing	10^{-2} x 10^{-4}	0-50	volatile weak acids	
• divalent cation (water hardness)	liquid	10^0 x 10^{-6}	0-50	max level * (M) at 10^{-3} M $\text{Ca}^{++}/\text{Mg}^{++}$ $\begin{cases} 3 \times 10^{-2} \text{ Na}^+; \\ 3 \times 10^{-5} \text{ Cu}^{++}, \text{Zn}^{++}; \\ 6 \times 10^{-5} \text{ Fe}^{++}; 10^{-4} \text{ Ni}^{++}; \\ 4 \times 10^{-4} \text{ Sr}^{++}; \\ 6 \times 10^{-4} \text{ Ba}^{++} \end{cases}$	
• fluoroborate	liquid	saturated to 3×10^{-6}	0-50	max level * (M) at 10^{-3} M BF_4^- $\begin{cases} 2 \times 10^{-2} \text{ NO}_3^-; 0.2 \text{ Br}^-; \\ \text{OAc}^-, \text{HCO}_3^-, \text{F}^-, \text{Cl}^-, \\ \text{OH}^-, \text{SO}_4^{--} \end{cases}$	
• hydrogen sulfide	gas sensing	10^{-2} to 10^{-6}	0-50	none	
• lead	solid-state	10^0 to 10^{-7}	0-80	max level: Ag^+ , Hg^{++} , $\text{Cu}^{++} < 10^{-7}$ M; high levels of cadmium and ferric ion interfere	can also be used to measure sulfate by titration with lead
• nitrogen oxide (nitrite)	gas sensing	10^{-2} to 5×10^{-7}	0-50	max level * (M) in 10^{-3} M NOx : CO_2 , 3×10^{-2} M; volatile weak acids interfere	measures NO and NO_2 in air after scrubbing
• pH	glass	pH 0-14	0-100	sodium interferes at pH 14	not to be used in acid fluoride solutions
• potassium	liquid	10^0 to 10^{-5}	0-50	max level * (M) at 10^{-3} M K^+ $\begin{cases} 10^{-4} \text{ Cs}^+; 3 \times 10^{-3} \text{ NH}_4^+; \\ 10^{-2} \text{ H}^+, \text{Ti}^+; 0.1 \text{ Ag}^+; 0.5 \text{ Na}^+ \end{cases}$	
• redox	combination	not applicable	0-80	not applicable	
• silver/sulfide	solid-state	10^0 to 10^{-7} Ag^+ or S^{--}	0-80	max level: $\text{Hg}^{++} < 10^{-7}$ M	
• sodium	solid-state	saturated to 10^{-6}	0-80	max level * (M) at 10^{-3} M Na^+ $\begin{cases} 3 \times 10^{-7} \text{ Ag}^+; 10^{-6} \text{ H}^+; \\ 5 \times 10^{-5} \text{ Li}^+; \\ 6 \times 10^{-2} \text{ Cs}^+; 0.1 \text{ K}^+; \\ 0.2 \text{ N}(\text{C}_2\text{H}_5)^+, 0.5 \text{ Ti}^+ \end{cases}$	10^{-8} lower limit possible with proper pH adjustment
	combination	saturated to 10^{-6}	0-80	same as solid state	
• sulfur dioxide (sulfite)	gas sensing	10^{-2} to 3×10^{-6}	0-50	max level * in 10^{-3} M SO_2 solution: HF , 3×10^{-3} M; acetic acid, 5×10^{-3} M; $\text{HCl} > 1$ M	for measuring SO_2 in stack gases

*For 10 percent error

TITLE DETERMINATION OF CATIONS USING SPECIFIC ION ELECTRODES (SIE) (CONTINUED)

ID NO. 02-02-01-18

B) BACKGROUND INFORMATION

- 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA 625/6-74-003, Cincinnati, 1974, p. 65-67.
- 223 Crosby, N.T., A.L. Dennis and J.G. Stevens, "An Evaluation of Some Methods for the Determination of Fluoride in Potable Waters and Other Aqueous Solutions," Analyst, 93(10), 643 (1968).
- 224 Tackett, S.L., "Automatic Titration of Calcium with EDTA Using a Calcium Selective Electrode," Anal. Chem., 41(12), 1703 (1969).
- 225 Muller, D.C., R.H. Muller and P.W. West, "Determination of Silver Ion in Parts per Billion Range with a Selective Ion Electrode," Anal. Chem., 41(14), 2038 (1969).
- 226 Baumann, E.W., "Determination of Aluminum by Potentiometric Titration with Fluoride," Anal. Chem., 42(1), 110 (1970).
- 227 Hadjiioannou, T.P., and D.S. Papastathopoulos, "EDTA Titration of Calcium and Magnesium with a Calcium-Selective Electrode," Talanta, 17, 399 (1970).

C) FIELD APPLICATIONS

- 228 Lee, T.G., "A System for Continuously Monitoring Hydrogen Chloride Concentrations in Gaseous Mixtures Using a Chloride Ion Selective Electrode," Anal. Chem., 41(2), 391 (1969).
- 229 Hicks, J.E., J.E. Fleenor and H.R. Smith, "The Rapid Determination of Sulfur in Coal," Anal. Chim. Acta., 68, 480 (1974).

1. TITLE DETERMINATION OF AMMONIA BY COLORIMETRIC PHENATE METHOD		2. IDENTIFICATION CODE 02-02-01-19
3. ABSTRACT OF METHODOLOGY		
The sample is treated with sodium phenolate and sodium hypochlorite solutions. The ammonia which is present reacts to form indophenol blue. The color formed is then intensified by the addition of sodium nitroprusside. The indophenol blue is determined spectrophotometrically at 630 nm; concentration is determined by comparison to standard curves. Sample pretreatments include the masking of calcium and magnesium ions with a 5% EDTA solution and/or filtration to minimize turbidity.		
4. APPLICATION: Compliance		
A) OPERATIONAL SCOPE Method is applicable to determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Calcium and magnesium ions interfere, but are removed with EDTA. Mercury chloride, used as preservative, gives negative interference by complexing with ammonia; this is overcome by addition of HgCl_2 to ammonia standards used in preparation of the standard curve. Turbidity and excessive color may also interfere. C) RECOMMENDED USE AREA This is the recommended compliance method for inorganic ammonia.		
5. OPERATIONAL PARAMETERS		
A) RANGE 0.01 to 2.0 mg/liter ammonia as nitrogen. B) ACCURACY In a single laboratory with surface water samples of 0.16 and 1.44 mg NH_3 as nitrogen per liter, recoveries were 107% and 99%, respectively. C) PRECISION Standard deviation of ± 0.005 was obtained in a single laboratory with 1.41, 0.77, 0.59 and 0.43 mg ammonia as nitrogen.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
High purity water, 5N sulfuric acid, sodium phenolate solution, sodium hypochlorite solution, disodium ethylenediamine tetraacetate (5%), sodium nitroprusside solution (0.05%), stock ammonium chloride solution.	Spectrophotometer for use at 630 nm with path length of 1 cm.	
8. KEYWORD INDEX: Ammonia, spectrophotometry, phenate method.		
9. CROSS REFERENCE ID NUMBERS 01-02; 02-02-01-20.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA-625/6-74-003, Washington, 1974, p. 168. 204 Taras, H.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, p. 232. B) BACKGROUND INFORMATION 186 Mitre Corporation, Compendium of Analytical Methods, Vol. II, Method Summaries, U.S. Environmental Protection Agency, PB 228-425, April 1973. 219 Rossum, J.R., and P.A. Villaruz, "Determination of Ammonia by the Indophenol Method," <i>J.A.W.W.A.</i>, 55, 657 (1963). 230 Weatherburn, M.W., "Phenol-Hypochlorite Reaction for Determination of Ammonia," <i>Anal. Chem.</i>, 39, 971 (1967). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL NITROGEN BY KJELDAHL METHOD	2. IDENTIFICATION CODE 02-02-01-20
3. ABSTRACT OF METHODOLOGY	
Total Kjeldahl nitrogen is the sum of free ammonia and organic nitrogen compounds (amino acids, proteins, possibly amines, nitro compounds, and hydrazones) which are converted to ammonium sulfate under the prescribed digestion conditions. The sample is heated in the presence of concentrated sulfuric acid, potassium sulfate and mercurous sulfate and evaporated until sulfur trioxide fumes evolve and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and treated with a hydroxide-thiosulfate solution. The ammonia is then distilled into 2% boric acid solution. Then NH_3 is determined by titration with standard sulfuric acid to a pH endpoint of 6.8 (see 02-02-01-19 for colorimetric finish, 02-02-01-18 for specific ion electrode finish) using methyl red/methylene blue mixed indicator.	
4. APPLICATION: Compliance	
A) OPERATIONAL SCOPE Method is applicable to determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Samples which are preserved by addition of concentrated sulfuric acid or mercuric chloride should be analyzed as soon as possible. C) RECOMMENDED USE AREA This is the recommended compliance method for total nitrogen.	
5. OPERATIONAL PARAMETERS	
A) RANGE 1 mg nitrogen/liter or above if titrimetric determination is performed; below 1 mg/liter if colorimetry is used. B) ACCURACY Accuracy as mg N/liter of +0.03, +0.02, +0.04 and -0.08 was obtained on samples containing 0.20, 0.31, 4.10 and 4.61 mg N/liter, respectively. C) PRECISION Precision as standard deviation of 0.197, 0.247, 1.056 and 1.191 was obtained on samples cited above.	
6. REAGENTS REQUIRED High purity water, sulfuric acid-mercuric sulfate-potassium sulfate solution; standard sulfuric acid solution, methyl red-methylene blue indicator.	7. EQUIPMENT REQUIRED Kjeldahl distillation apparatus, consisting of Kjeldahl flask, bulb or trap, and vertical condenser titration assembly, spectrophotometer for use at 425 nm.
8. KEYWORD INDEX: Nitrogen (total), Kjeldahl, titrimetry, colorimetry.	
9. CROSS REFERENCE ID NUMBERS 01-02; 02-02-01-19, 02-02-01-18.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA-625/6-74-003, Washington, 1974, p. 175. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, p. 232. B) BACKGROUND INFORMATION 186 Mitre Corporation, "Compendium of Analytical Methods, Volume II, Method Summaries," U.S. Environmental Protection Agency, PB-228-425, April 1973, p. 8-36. 231 Kjeldahl, J., "A New Method for the Determination of Nitrogen in Organic Matter," <i>Z. Anal. Chem.</i>, 22, 366 (1883).	

TITLE DETERMINATION OF TOTAL NITROGEN BY KJELDAHL METHOD (CONTINUED)

ID NO. 02-02-01-20

B) BACKGROUND INFORMATION (Continued)

232 Mackenzie, H.A., and H.S. Wallace. "The Kjeldahl Determination of Nitrogen: A Critical Study of Digestion Conditions," *Austral. J. of Chem.*, 7, 55 (1954).

233 Boltz, D.F. (ed.), "Colorimetric Determination of Nonmetals," Interscience Publishers, New York, p. 75-97, 1958.

C) FIELD APPLICATIONS

2. IDENTIFICATION CODE

02-02-01-21

1. TITLE DETERMINATION OF HEAVY METALS BY DITHIZONE METHOD

3. ABSTRACT OF METHODOLOGY

Diphenylthiocarbazone (dithizone) reacts to form colored coordination compounds with silver, cadmium, lead, zinc and other heavy metals. Under the proper conditions and with removal of interferences, the reaction can be made selective for a desired metal. Table 02-02-01-21A lists specific procedures for removal of interferences for Ag, Cd, Pb and Zn. The colored metal-dithizone complexes are then measured spectrophotometrically and specific concentrations are obtained from calibration curves prepared from standard solutions. Dithizone solutions must be purified by filtration and extraction with aqueous ammonium hydroxide in order to remove oxidation contaminants (diphenylthiocarbonyl diazone).

4. APPLICATION: Engineering evaluation R&D.

A) OPERATIONAL SCOPE

Method is applicable to heavy metal determinations in drinking, surface and saline waters, domestic and industrial wastes.

B) INTERFERENCES/LIMITATIONS

See Table 02-02-01-21A for complete list of interferences. Dithizone solutions are decomposed by sunlight and in the light beam of the spectrophotometer. Because of the extreme sensitivity of the method, all glassware used in the determinations should be thoroughly cleaned with high purity water and segregated from other glassware prior to use.

C) RECOMMENDED USE AREA

This is an engineering evaluation R&D procedure for the determination of heavy metals in aqueous effluents.

5. OPERATIONAL PARAMETERS

A) RANGE See Table 02-02-01-21A.

B) ACCURACY The following relative errors have been determined: For Ag, 66.6%; for Zn, 25.9%; for Pb, 8.5%.

C) PRECISION The following relative standard deviations have been obtained: For Ag, 61.0%; for Zn, 18.2%; for Pb, 42.1%.

6. REAGENTS REQUIRED

See Table 02-02-01-21A.

7. EQUIPMENT REQUIRED

Spectrophotometer; standard laboratory glassware for filtrations, extractions.

8. KEYWORD INDEX: Heavy metals, dithizone, spectrophotometry.

9. CROSS REFERENCE ID NUMBERS 01-02-01, 02; 02-02-01-01.

10. REFERENCES

A) PRIMARY SOURCE

204 American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, "Standard Methods for the Examination of Waste and Wastewater," 13th ed., Washington, D. C., 1971, 174 pp.

B) BACKGROUND INFORMATION

186 Mitre Corporation, "Compendium of Analytical Methods, Vol. II, Method Summaries," EPA PB 228-425, April 1973.

C) FIELD APPLICATIONS

TITLE DETERMINATION OF HEAVY METALS BY DITHIZONE METHOD (CONTINUED)

ID NO. 02-02-01-21

Table 02-02-01-21A. (Reference 204).

Metal	Minimum Detectable Concentration (µg)	Interferences	Procedures for Removal of Interferences	Analytical λ (nm)
Ag	0.2	Ferric ions, residual chlorine, other oxidizing agents	Ferric ion is removed by extraction with aqueous ammonium thiocyanate reagent; sample is digested with sulfuric acid, urea, hydroxylamine sulfate.	620
Cd	0.5	Ag, Hg, Cu, Ni, Co interfere in basic solutions; organic material interferes	Organics are decomposed by digestion with HNO ₃ -H ₂ SO ₄ ; Cl is precipitated with AgNO ₃ . Cu, Ag and Hg are extracted with dithizone in CHCl ₃ , pH 2. After adjustment to pH 9, Ni and Co are removed by dimethylglyoxime. At pH 14, Zn and Cd are extracted with dithizone in CHCl ₃ ; Zn is then removed by NaOH wash.	515
Zn	1.0	Heavy metals	Sample is adjusted to pH 4-5.5; sodium thiosulfate is added, with acetate buffer.	535 or 620
Pb	2.0	Heavy metals, particularly tin; organic material	Organics are removed by acid digestion or ignition. Sn is removed by volatilization as SnBr ₄ . For removal of other metals, sample is extracted with ammonium citrate - hydroxylamine hydrochloride; then is made alkaline; KCN is added and pH is adjusted to 8.5 to 9. Then ammoniacal cyanide-citrate reagent is added to complex remaining heavy metal interferences.	510

1. TITLE DETERMINATION OF HEXAVALENT CHROMIUM BY DIPHENYL CARBAZIDE METHOD	2. IDENTIFICATION CODE 02-02-01-22
3. ABSTRACT OF METHODOLOGY	
Hexavalent chromium can be determined by treatment with an acidic solution of s-diphenyl carbazide reagent. A reddish purple complex is formed, which can be measured spectrophotometrically at 540 nm. The concentration of the sample is obtained using calibration curves prepared from standard solutions.	
4. APPLICATION: Environmental assessment, engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Mercury interferes by producing a blue-purple color, but the reaction is not extensive at the acidity level used. Iron at concentrations greater than 1 mg/liter interferes by producing a yellow color. Vanadium also interferes, but the color produced fades rapidly (10 minutes). Sample must be analyzed rapidly once the reagent is added, or low chromium values will be obtained. C) RECOMMENDED USE AREA This method is applicable to environmental assessment if specific valence state information about Cr is required.	
5. OPERATIONAL PARAMETERS	
A) RANGE Minimum detectable concentration is 5 µg/liter when a 5 cm light path is used for photometric measurement. B) ACCURACY Accuracy is dependent upon the promptness of analysis. C) PRECISION Photometric measurements in the range below 400 µg/liter can be made with a precision of 10 µg/liter Cr.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
High purity water; s-diphenyl carbazide in ethyl or isopropyl alcohol with sulfuric acid; standard chromium solutions.	Spectrophotometer for use at 540 nm; standard laboratory glassware.
8. KEYWORD INDEX: Chromium, diphenyl carbazide; spectrophotometry.	
9. CROSS REFERENCE ID NUMBERS 01-02-02, 01-02-01.	
10. REFERENCES	
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, p. 156. B) BACKGROUND INFORMATION 186 Mitre Corporation, "Compendium of Analytical Methods, Vol. II. Method Summaries," EPA, PB 228-425, April 1973, p. C-8. C) FIELD APPLICATIONS	

1. TITLE DETERMINATION OF IRON (TOTAL, FILTERABLE OR FERROUS) BY PHENANTHROLINE METHOD		2. IDENTIFICATION CODE 02-02-01-23
3. ABSTRACT OF METHODOLOGY For a determination of total iron, the sample iron is solubilized, then is reduced to the ferrous state by boiling with hydrochloric acid and hydroxylamine solution. The solution is then treated with ammonium acetate buffer and 2 ml phenanthroline. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. Total iron is then determined spectrophotometrically at 510 nm after the solution is allowed to stand 10-15 minutes. For a determination of filterable iron, the sample is filtered immediately after collection through a 0.45µ membrane filter into a vacuum flask containing dilute HCl. Total filterable iron is analyzed as described above. Filterable ferrous iron is determined by adding concentrated hydrochloric acid to the sample immediately after collection, followed by addition of phenanthroline and ammonium acetate solutions. The spectrophotometric measurements are then performed within 5 to 10 minutes after addition of reagents. Concentrations are determined by comparison to calibration curves prepared using standard reagents.		
4. APPLICATION: Environmental assessment, engineering evaluation R&D.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes.		
B) INTERFERENCES/LIMITATIONS Strong oxidizing agents interfere (cyanide, nitrite and phosphates; chromium and zinc in concentrations greater than 10 times iron; cobalt and copper in excess of 5 mg/liter and nickel in excess of 2 mg/liter). Initial boiling with acid and hydroxylamine solution eliminates these interferences. Excessive concentrations of metal ions or anions that complex iron, such as citrate, tartrate, oxalate and phosphate, can be eliminated by a preliminary extraction procedure or using tripyridine.		
C) RECOMMENDED USE AREA This method is applicable to environmental assessment when valence state information about Fe is required.		
5. OPERATIONAL PARAMETERS		
A) RANGE Minimum detectable concentration is 3µg spectrophotometrically using a 10-cm cell path length. Total, dissolved or ferrous iron concentrations between 0.02 and 4.0 mg/liter can be determined directly, and higher concentrations can be determined by the use of aliquots.		
B) ACCURACY Relative error of 13.3% was obtained in 44 laboratories on synthetic unknown samples containing 300µg/liter Fe.		
C) PRECISION A relative standard deviation of 25.5% was obtained using the sample described above.		
6. REAGENTS REQUIRED High purity water; concentrated hydrochloric acid; hydroxylamine solution; ammonium acetate buffer solution; 1, 10 - phenanthroline monohydrate, standard iron (ferric ammonium sulfate) solutions.	7. EQUIPMENT REQUIRED Spectrophotometer for use at 510 nm; standard laboratory glassware, including extraction funnels.	
8. KEYWORD INDEX: Iron, phenanthroline, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02, 02-02-01-05		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, p. 189.		
B) BACKGROUND INFORMATION 186 Mitre Corporation, "Compendium of Analytical Methods, Vol. II. Method Summaries," EPA PB 228 425, April 1973, p. C-20.		
C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF CHEMICAL OXYGEN DEMAND	2. IDENTIFICATION CODE 02-02-01-24
3. ABSTRACT OF METHODOLOGY Organic substances in the sample are oxidized by 0.250N potassium dichromate in 50% sulfuric acid solution at reflux temperature using silver sulfate as catalyst and mercuric sulfate to remove interferences by chloride. The excess dichromate is titrated with standard of 0.10N ferrous ammonium sulfate using orthophenanthroline ferrous complex as an indicator. For samples having an organic carbon concentration of less than 15 mg/liter, the Low Level Modification should be used, in which 0.025N potassium dichromate is used to oxidize the sample, and 0.01N ferrous ammonium sulfate is used in the back-titration. When the sample has a chloride concentration greater than 2,000 mg/liter, the Saline Water Modification should be used, in which a standard curve of COD versus mg/liter of chloride is prepared using sodium chloride solutions of varying concentrations, using the same procedure applied to the sample. A chloride range of 4,000 mg/liter to 20,000 mg/liter should be determined.	
4. APPLICATION: Compliance, environmental assessment	
A) OPERATIONAL SCOPE Method is applicable to domestic and industrial waste samples having an organic carbon concentration greater than 15 mg/liter. B) INTERFERENCES/LIMITATIONS Chloride interferes, but is removed by addition of mercuric sulfate. There is a risk of loss of volatile organics, which is minimized by cooling the flask during the sulfuric acid addition. C) RECOMMENDED USE AREA This is the COD compliance test.	
5. OPERATIONAL PARAMETERS	
A) RANGE Method is applicable to waste samples having an organic carbon concentration greater than 15 mg/l. For lower concentrations of carbon (as in surface waters), or for very high concentrations of chloride (>2,000 mg/l), procedural modifications are required (see Abstract of Methodology). B) ACCURACY Accuracy as percent relative error (bias) of -4.7% has been reported. C) PRECISION Standard deviation of +17.76 mg/l COD reported for analyses conducted in over 50 laboratories.	
6. REAGENTS REQUIRED Potassium dichromate solution, sulfuric acid, standard ferrous ammonium sulfate titrant.	7. EQUIPMENT REQUIRED Reflux apparatus.
8. KEYWORD INDEX: Chemical oxygen demand (COD), aqueous effluents, dichromate oxidation	
9. CROSS REFERENCE ID NUMBERS 01-02-02; 01-02-01	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 20. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 220, p. 495. B) BACKGROUND INFORMATION 492 Moore, W.A., F.J. Ludzack and C.C. Ruchhoft, "Dichromate Reflux Method for Determining Oxygen Consumed," <i>Anal. Chem.</i>, 21, 953 (1949). 493 Medalla, A.I., "Test for Traces of Organic Matter in Water," <i>Anal. Chem.</i>, 23, 1318 (1951). 494 Symons, J.M., H.H. Hassis and R.E. McKinney, "A Procedure for Determination of Biological Treatability of Industrial Wastes," <i>J.W.P.C.F.</i>, 32, 841 (1960). C) FIELD APPLICATIONS 495 Miers, H.M., "Biological Purification of Whey Solutions," <i>J. Soc. Chem. Ind.</i>, 55, 711 (1936).	

1. TITLE DETERMINATION OF AMMONIA BY DISTILLATION PROCEDURE		2. IDENTIFICATION CODE 02-02-01-25
3. ABSTRACT OF METHODOLOGY		
The sample is buffered at pH 9.5 with a borate buffer to minimize hydrolysis of cyanates and organic nitrogen compounds. The sample is then distilled into a boric acid solution. The ammonia present in the distillate is then determined by Nesslerization, or potentiometrically using an ammonia electrode, or by titration with sulfuric acid with a mixed indicator (see 02-02-01-19). Prior to analysis, the samples may be preserved with 2 ml conc. H_2SO_4 or 10 mg/l $HgCl_2$ and stored at 4°C.		
4. APPLICATION: Compliance, environmental assessment		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Residual chlorine interferes but can be removed by addition of sodium thiosulfate prior to distillation. Volatile alkaline compounds (formaldehyde, certain ketones, and alcohols) may interfere with Nesslerization; these may be boiled off at pH 2-3 prior to distillation. If necessary, mercury salts are used to preserve the sample; these must be removed prior to distillation by addition of sodium thiosulfate. C) RECOMMENDED USE AREA This is an NH_3 compliance test.		
5. OPERATIONAL PARAMETERS		
A) RANGE 0.05-1.0 mg/l NH_3 nitrogen for the colorimetric procedure; 1.0-25 mg/l for the titrimetric procedure; 0.05-1400 mg/l for the electrode method. B) ACCURACY A study conducted by 24 analysts in 16 laboratories resulted in accuracies (as bias, mg N/liter) of -0.05 to +0.01 for samples having 0.21 to 1.92 mg N/liter. C) PRECISION In the study described above, precisions ranging from 0.070 to 0.279 mg N/liter were achieved.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Ammonium chloride, borate buffer, mixed indicator (methyl red, methylene blue); Nessler reagent (mercuric iodide, potassium iodide), sulfuric acid, sodium hydroxide.	Kjeldahl flask, Erlenmeyer flasks, Nessler tubes, spectrophotometer.	
8. KEYWORD INDEX: Ammonia, distillation, Nesslerization, titrimetry, potentiometry		
9. CROSS REFERENCE ID NUMBERS 02-02-01-19; 02-02-01-20; 01-02-01; 01-02-02		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 159. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 132, p. 224. B) BACKGROUND INFORMATION 496 Jackson, D.D., "Permanent Standards for Use in the Analysis of Water," <i>Massachusetts Inst. Technol. Quart.</i>, 13, 314 (1900). 497 Nichols, M.S., and M.E. Fotte, "Distillation of Free Ammonia from Buffered Solutions," <i>Ind. Eng. Chem., Anal. Ed.</i>, 3, 311 (1931). 498 Sawyer, C.N., "pH Adjustment for Determination of Ammonia Nitrogen," <i>Anal. Chem.</i>, 25, 816 (1953). 219 Rossum, J.R., and P.A. Villarruz, "Determination of Ammonia by the Indophenol Method," <i>J. Am. Water Works Assoc.</i>, 55, 657 (1963).		

1. TITLE DETERMINATION OF BERYLLIUM BY ALUMINON METHOD	2. IDENTIFICATION CODE 02-02-01-26
3. ABSTRACT OF METHODOLOGY	
Method involved pre-addition of ethylenediamine titraacetic acid (EDTA) to eliminate interference of aluminum, cobalt, copper, iron, manganese, nickel, titanium, zinc, and zirconium. The sample is then treated with aluminon buffer reagent and the colored beryllium complex formed is determined spectrophotometrically at 515 nm.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS As indicated above, interferences due to aluminum, cobalt, copper, iron, manganese, nickel, titanium, zinc, and zirconium are removed with addition of EDTA. C) RECOMMENDED USE AREA This colorimetric method is useful as an alternate to the AAS procedure (see 02-02-01-05).	
5. OPERATIONAL PARAMETERS	
A) RANGE Minimum detectable concentration is 5 µg/liter. B) ACCURACY N/Q C) PRECISION N/Q	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
EDTA reagent, aluminon buffer reagent, beryllium stock solution.	Spectrophotometer for use at 515 nm, standard laboratory glassware.
8. KEYWORD INDEX: Beryllium, aqueous effluents, aluminon, spectrophotometry	
9. CROSS REFERENCE ID NUMBERS 01-02-01; 01-02-02, 02-02-01-05.	
10. REFERENCES	
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 106B, p. 67. B) BACKGROUND INFORMATION 499 Luke, C.L., and M.E. Campbell, "Photometric Determination of Beryllium in Beryllium-Copper Alloys," <i>Anal. Chem.</i>, 24, 1056 (1952). 500 Luke, C.L., and K.C. Brown, "Photometric Determination of Aluminum in Manganese, Bronze, Zinc Die Casting Alloys, and Magnesium Alloys," <i>Anal. Chem.</i>, 24, 1120 (1952). C) FIELD APPLICATIONS	

1. TITLE DETERMINATION OF TOTAL CHROMIUM BY DIPHENYL CARBAZIDE METHOD		2. IDENTIFICATION CODE 02-02-01-27
3. ABSTRACT OF METHODOLOGY		
The determination of total chromium involves the oxidation of chromium to the hexavalent state, followed by complexation with diphenyl carbazide and spectrophotometric measurement at 540 nm (see 02-02-01-22). The sample is first digested with an $H_2SO_4-HMnO_3$ or HNO_3-HClO_4 mixture in order to decompose organic matter, then is adjusted to 0.5N acidity. Potassium permanganate is next added to oxidize the chromium to Cr^{+6}. Sodium oxide is added to reduce excess permanganate. Finally, the diphenyl carbazide reagent is added and the red-violet complex is determined spectrophotometrically.		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Vanadium interferes at concentrations greater than ten times the chromium concentration. Vanadium, molybdenum, iron and copper can be removed by extraction into chloroform. Hexavalent Hg will also form a colored complex with the reagent, but its intensity is lower than that for chromium at the specified pH. C) RECOMMENDED USE AREA This is an alternate compliance test for total chromium.		
5. OPERATIONAL PARAMETERS		
A) RANGE 10 µg/liter using 100 ml aliquotes of sample. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Sodium azide, diphenyl carbazide, potassium permanganate, sulfuric acid, nitric acid.	Spectrophotometer for use at 540 nm standard laboratory glassware.	
8. KEYWORD INDEX: Total chromium, aqueous effluents, diphenyl carbazide, permanganate oxidation		
9. CROSS REFERENCE ID NUMBERS 02-02-01-22; 01-02-01; 01-02-02, 02-02-01-05		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J., ed., "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th Edition, Method 211C, 1971, p. 426. B) BACKGROUND INFORMATION 186 Mitre Corporation, "Compendium of Analytical Methods, Vol. II., Method Summaries," EPA PB 228-425, April, 1973, p. C-8. 501 Rowland, G.P., Jr., "Photo Electric Colorimetry-Optical Study of Permanganate Ion and of Chromium-Diphenylcarbazide System," Anal. Chem., 11, 442 (1939). 502 Saltzman, B.E., "Microdetermination of Chromium with Diphenylcarbazide by Permanganate Oxidation," Anal. Chem., 24, 1016 (1952). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL COPPER BY NEOCUPROINE METHOD		2. IDENTIFICATION CODE 02-02-01-28
3. ABSTRACT OF METHODOLOGY The determination of total copper involves preliminary sample digestion to remove organics and interfering anions, followed by treatment of the sample with hydroxylamine hydrochloride to reduce copper to Cu^{+2} and with sodium citrate for prevention of complexation by interfering metal ions. Following pH adjustment (to pH 3-9) by addition of ammonia, the neocuproine reagent is added and the resultant complex is extracted with chloroform-methanol solution, and determined spectrophotometrically at 457 nm.		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes.		
B) INTERFERENCES/LIMITATIONS Interference from chromium can be reduced by the addition of sulfurous acid. Cyanide, sulfide and organics interfere, but are removed during digestion.		
C) RECOMMENDED USE AREA This is an alternative compliance method for Cu (see 02-02-01-05).		
5. OPERATIONAL PARAMETERS		
A) RANGE 30 $\mu\text{g/liter}$ using a 100 ml sample aliquot and 1 cm cell; 6 $\mu\text{g/liter}$ using a 100 ml sample aliquot and 5 cm cell.		
B) ACCURACY N/Q		
C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Redistilled water, conc. sulfuric acid, 60% perchloric acid, hydroxylamine hydrochloride solution, sodium citrate solution, ammonium hydroxide, 2,9-dimethyl-1,10-phenanthroline hemihydrate.		Spectrophotometer for use at 457 m μ , standard laboratory glassware, separatory funnels.
8. KEYWORD INDEX: Total copper, aqueous effluents, phenanthroline, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-23, 02-02-01-05		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 211E, p. 430.		
B) BACKGROUND INFORMATION 503 Smith, G.F., and W.H. McCurdy, "2,9-Dimethyl-1,10-Phenanthroline; New Specific Reagent in Spectrophotometric Determination of Copper," <i>Anal. Chem.</i> , 24, 371 (1952). 504 Gahler, A.R., "Colorimetric Determination of Copper with Neocuproine," <i>Anal. Chem.</i> , 26, 577 (1954). 505 Fulton, J.W., and J. Hastings, "Photometric Determinations of Copper in Aluminum and Lead-Tin Solder with Neocuproine," <i>Anal. Chem.</i> , 28, 174 (1956). 506 Frank, A.J., A.A. Deacutis and A.B. Goulston, "Spectrophotometric Determination of Copper in Titanium," <i>Anal. Chem.</i> , 29, 750 (1957).		
C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF CALCIUM BY GRAVIMETRIC METHOD		2. IDENTIFICATION CODE 02-02-01-28
3. ABSTRACT OF METHODOLOGY		
Method involves the precipitation of calcium in the sample with ammonium oxalate to form calcium oxalate. The precipitation is accomplished in several stages with pH adjustments in order to maximize the amount of precipitate formed. The precipitate formed is ignited and weighed as calcium oxide. The filtrate from the determination is used for the determination of total magnesium (see 02-02-01-30).		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Silica interferes, and can be removed by treatment with HCl. Aluminum iron and manganese interfere, but can be precipitated with ammonium hydroxide. Suspended matter should also be removed by centrifuging or filtration. C) RECOMMENDED USE AREA This is an alternative engineering evaluation R&D procedure for Ca^{+2} when large quantities of Ca^{+2} are expected (see 02-02-01-05)		
5. OPERATIONAL PARAMETERS		
A) RANGE Samples or sample aliquots containing up to 250 mg Ca per 200 ml solution can be analyzed using this method. B) ACCURACY A synthetic sample containing 108 mg/l Ca was determined in four laboratories, with a relative error of 1.9%. C) PRECISION The determination on the sample described above gave a relative standard deviation of 3.7%.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Ammonium oxalate, ammonium hydroxide, ammonium persulfate, and ammonium chloride, hydrochloric acid for interference removals.		Standard laboratory glassware, platinum crucible, desiccator, analytical balance.
8. KEYWORD INDEX: Calcium aqueous effluents, gravimetry, ammonium oxalate.		
9. CROSS REFERENCE ID NUMBERS 02-02-01-30; 01-02-01, 01-02-02; 02-02-01-12, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 110A, p. 80. B) BACKGROUND INFORMATION 507 Willard, H.H., C.E. Bricker and N.H. Furman, "Elements of Quantitative Analysis," 4th ed., D. Van Nostrand Co., Princeton, N.J., 1956. 508 Kolthoff, I.M., S. Bruckenstein, E.J. Meehan and E.B. Sandell, "Quantitative Chemical Analyses," 4th ed., Macmillan Co., New York, 1969. 509 Ingals, R.S., and P.E. Murray, "Urea Hydrolyses for Precipitating Calcium Oxalate," Anal. Chem., 21, 525 (1949). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL MAGNESIUM BY GRAVIMETRIC METHOD		2. IDENTIFICATION CODE 02-02-01-30
3. ABSTRACT OF METHODOLOGY Using the filtrate from 02-02-01-30, magnesium is determined by precipitation with diammonium hydrogen phosphate to give magnesium ammonium phosphate. The precipitate is then ignited and determined as magnesium pyrophosphate. Prior to the actual precipitation, the sample is treated with concentrated nitric acid for the removal of ammonium salts and oxalate. If this pretreatment is not performed, the sample can be double-precipitated to ensure complete removal of magnesium. Magnesium can be determined by the gravimetric method only after prior removal of calcium salts; this method is usually performed on the filtrate and washings from the gravimetric calcium determination (see 02-02-01-29).		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes.		
B) INTERFERENCES/LIMITATIONS Aluminum, calcium, iron, manganese, silica, strontium, and suspended matter interfere. The solution should contain less than 3.5-g NH_4Cl .		
C) RECOMMENDED USE AREA This is an alternative compliance test for Mg (see 02-02-01-05 for primary method).		
5. OPERATIONAL PARAMETERS		
A) RANGE To several hundred mg/l.		
B) ACCURACY A synthetic sample containing 82 mg/l magnesium was determined in eight separate laboratories with a relative error of 4.9%.		
C) PRECISION The determinations on the sample described above gave a relative standard deviation of 6.3%.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Nitric acid, hydrochloric acid, methyl red indicator solution, diammonium hydrogen phosphate solution, ammonium hydroxide.		Standard laboratory glassware, crucible.
8. KEYWORD INDEX: Total magnesium, aqueous effluents, gravimetry, diammonium hydrogen phosphate.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-29, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971. Method 127A, p. 201.		
B) BACKGROUND INFORMATION 510 Epperson, A.W., "The Pyrophosphate Method for the Determination of Magnesium and Phosphoric Anhydride," J. Amer. Chem. Soc., 50, 321 (1928). 508 Kolthoff, I.M. and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed., Macmillan Co., New York, Chapter 22. 511 Hillebrand, W.F., et al, "Applied Inorganic Analysis," 2nd ed., John Wiley & Sons, Inc., New York, Chapter 41, p. 133-134.		
C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF NICKEL BY HEPTOXIME METHOD		2. IDENTIFICATION CODE 02-02-01-31
3. ABSTRACT OF METHODOLOGY		
Method involves preliminary digestion of the sample with a $\text{HNO}_3\text{-H}_2\text{SO}_4$ mixture, then treatment with cupferron reagent. The iron and copper cupferrates formed are then removed from the sample by extraction with chloroform. The sample is then treated with 1,2-cycloheptanedionedioxime, and the nickel heptoxime complex formed is extracted with chloroform, reextracted into the aqueous phase with hydrochloric acid and is determined spectrophotometrically at 445 nm.		
4. APPLICATION: Compliance		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Iron and copper interfere, but are removed by preliminary treatment of the sample with cupferron reagent. C) RECOMMENDED USE AREA This is an alternate Ni compliance test (see 02-02-01-05).		
5. OPERATIONAL PARAMETERS		
A) RANGE To several hundred mg/l. B) ACCURACY N/Q C) PRECISION No precision data are available.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
1,2-cycloheptanedionedioxime (heptoxime reagent); cupferron solution, nitric acid, sulfuric acid, hydroxylamine hydrochloride solution.		Spectrophotometer for use at 445 nm, separating funnels, standard laboratory glassware.
8. KEYWORD INDEX: Nickel, aqueous effluents, heptoxime method, colorimetry.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 211(11)I, p. 443. B) BACKGROUND INFORMATION 512 Butts, P.G., A.R. Gahler, and M.G. Mellon, "Colorimetric Determination of Metals in Sewage and Industrial Wastes," <i>Sewage & Ind. Wastes</i>, 22, 1543 (1950). 513 Ferguson, R.C., and C.V. Banks, "Spectrophotometric Determination of Nickel Using 1,2-Cycloheptanedionedioxime (heptoxime)," <i>Anal. Chem.</i>, 23, 448 and 1486 (1951). 514 Serfass, E.J., and R.F. Merraca, "Procedures for Analyzing Metal Finishing Wastes," Ohio River Valley Water Sanitation Commission, Cincinnati, Ohio, 1954. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF POTASSIUM BY COBALTNITRITE METHOD		2. IDENTIFICATION CODE 02-02-01-32
3. ABSTRACT OF METHODOLOGY		
Method involves precipitation of potassium with trisodium cobaltinitrite, followed by oxidation of the dipotassium sodium cobaltinitrite formed with potassium dichromate and sulfuric acid. The excess dichromate is then determined colorimetrically at 425 nm. Since temperature and precipitation time affect the results, a series of standards containing known potassium concentrations should be run simultaneously with the samples.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Ammonium ion interferes. Silica may interfere if silica gel forms during the evaporation and addition of the reagent. The gel can be removed by filtration. No other common ions interfere. C) RECOMMENDED USE AREA This is an alternate colorimetric engineering evaluation R&D procedure for cobalt (see 02-02-01-05).		
5. OPERATIONAL PARAMETERS		
A) RANGE Samples of 100 to 700 mg/liter potassium can be determined, using 10 ml aliquots. B) ACCURACY ± 0.5 mg potassium. C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Trisodium cobaltinitrite, potassium dichromate, nitric acid, sulfuric acid, standard potassium stock solution.	Spectrophotometer for use at 425 nm, centrifuge, standard laboratory glassware.	
8. KEYWORD INDEX: Potassium aqueous effluents, spectrophotometry, sodium cobaltinitrite.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 147B, p. 285. B) BACKGROUND INFORMATION 515 Wander, I.W., "Photometric Determination of Potassium," <i>Ind. Eng. Chem., Anal. Ed.</i>, 14, 471 (1942). 508 Kolthoff, I.M., S. Bruckenstein, E.J. Meenez and E.B. Sandell, "Quantitative Chemical Analysis," 4th ed., Macmillan Co., New York, 1969. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF VANADIUM BY GALLIC ACID METHOD		2. IDENTIFICATION CODE 02-02-01-33
3. ABSTRACT OF METHODOLOGY Method involves treatment of the sample with gallic acid and ammonium persulfate-phosphoric acid reagent. The vanadium catalyzes the oxidation of the gallic acid by persulfate; the extent of oxidation is proportional to the vanadium concentration present in the sample. The vanadium is determined by spectrophotometric measurement of the sample at 415 nm and comparison to a calibration curve plotted using standards prepared in the same way as the sample but having known concentrations of vanadium.		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes.		
B) INTERFERENCES/LIMITATIONS The following ions interfere: Cr^{+6} (1.0 mg/l); Co^{+2} (1.0 mg/l); Cu^{+2} (0.05 mg/l); Fe^{+2} (0.3 mg/l); Fe^{+3} (0.5 mg/l); Mo^{+6} (0.1 mg/l); Ni^{+2} (3.0 mg/l); Ag (2.0 mg/l); U^{+6} (3.0 mg/l); Br^- (0.1 mg/l); Cl^- (100.10 mg/l); I^- (0.001 mg/l). Addition of mercuric ion eliminates interferences due to Cl^- , Br^- , and I^- .		
C) RECOMMENDED USE AREA This is an alternate compliance test for vanadium (see 02-02-01-05).		
5. OPERATIONAL PARAMETERS		
A) RANGE Minimum detectable concentration is 0.025 μg .		
B) ACCURACY A synthetic sample containing 6 $\mu\text{g/l}$ of vanadium was determined in 22 laboratories with no relative error.		
C) PRECISION The determination on the sample described above gave a relative standard deviation of 20.		
6. REAGENTS REQUIRED Gallic acid solution, ammonium persulfate-phosphoric acid reagent, mercuric nitrate solution, standard vanadium solution.	7. EQUIPMENT REQUIRED Spectrophotometer for use at 415 nm, water bath ($25 \pm 0.5^\circ\text{C}$), standard laboratory glassware.	
8. KEYWORD INDEX: Vanadium, aqueous effluents, spectrophotometry, gallic acid.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02, 02-02-01-05.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971.		
B) BACKGROUND INFORMATION 516 Fishman, M.J., and M.V. Skougstad, "Catalytic Determination of Vanadium in Water," Anal. Chem., 36, 1643 (1964).		
C) FIELD APPLICATIONS		

1. TITLE METHOD FOR DETERMINATION OF TOTAL ALPHA RADIOACTIVITY USING PROPORTIONAL OR SCINTILLATION COUNTERS		2. IDENTIFICATION CODE 02-02-01-34
3. ABSTRACT OF METHODOLOGY Method involves determination of alpha radioactivity by means of proportional or scintillation counters, which consist of detecting devices, amplifiers, power supplies, and scalers. Alpha particles which enter the proportional detector ionize the counting gas; the negative ions produced are accelerated toward the anode and ionize additional counting gas, resulting in a voltage pulse. In the scintillation detector, the alpha particles excite atoms of a phosphor material; the release of light quanta by these excited atoms are detected and transformed into voltage impulses in a photomultiplier tube. The number of pulses per unit time in both methods is related to the disintegration rate of the test sample. Samples are prepared for counting by evaporation of a suitable volume of sample solution and several ml. of concentrated nitric acid in a beaker on a hot plate or steam bath, followed by further drying in an oven or with a Bunsen burner. Alternatively, the sample may be precipitated in order to concentrate the radioactivity present into smaller amounts of material.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous effluents which emit alpha-emitting radioelements; method does not measure those radioelements that are volatile under the conditions of analysis. It is sensitive to alpha emissions above 3.9 MeV in energy and at activity levels above 0.5 pCi/ml of aqueous water. Method is useful for both absolute and relative determinations.		
B) INTERFERENCES/LIMITATIONS Solids interfere with detection; the solids content should remain constant among related test samples. A 10-15% loss in counting rate may be experienced due to 1 mg/cm ² solids content on the sample dish.		
C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE Maximum radioactivity determinable is 100,000 cpm; the limit of sensitivity is dependent on the background counting rate, which should be as low as possible.		
B) ACCURACY Not available at this time.		
C) PRECISION ±5%		
6. REAGENTS REQUIRED Reagent grade water, concentrated nitric acid.		7. EQUIPMENT REQUIRED Sample mounting discs or dishes, scintillation or proportional detector and scaler, Bunsen burner or oven (103 to 105°C), standard laboratory glassware.
8. KEYWORD INDEX: Radioactivity, aqueous effluents, proportional counter, scintillation counter, alpha radiation.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-35, 02-02-01-36.		
10. REFERENCES		
A) PRIMARY SOURCE 024 ASTM Committee D-19 and D-22, "Water: Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1443-66, "Standard Method for Measurement of Alpha Particle Radioactivity of Water," American Society for Testing and Materials, Philadelphia, PA., 1971, pp. 501-505. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 302, p. 598.		
B) BACKGROUND INFORMATION 517 Goldin, A.S., J.S. Nader and L.R. Setter, "The Detectability of Low-Level Radioactivity in Water," J. Am. Water Works Assoc. 45, 73 (1953). 518 Setter, L.R., A.S. Goldin and J.S. Nader, "Radioactivity Assay of Water and Industrial Wastes with Internal Proportional Counter," Anal. Chem., 26, 1304 (1954). 519 National Center for Radiological Health, "Radioassay Procedures for Environmental Samples," PHS Pub. No. 999-RH-27, U.S. Dept. of Health, Education and Welfare, Washington, D.C., Jan. 1967.		

1. TITLE METHOD FOR DETERMINATION OF TOTAL BETA RADIOACTIVITY USING PROPORTIONAL OR GEIGER-MULLER COUNTERS		2. IDENTIFICATION CODE 02-02-01-36
3. ABSTRACT OF METHODOLOGY		
Method involves determination of beta radioactivity by means of proportional or Geiger-Muller counters, which consist of a detector (internal or external proportional gas-flow chambers or Geiger-Muller tubes) and combined amplifier, power supply, and scaler. The proportional counter is preferred for samples having wide ranges of beta radioactivity (10 to 80,000 cpm). Beta particles which enter the detector ionize the counting gas; the resultant negative ions are accelerated toward the anode and ionize additional counting gas, resulting in a voltage pulse. The number of pulses per unit of time is related to the disintegration rate of the test sample. Samples are prepared for measurement by precipitation, ion exchange or evaporation methods. Measurement efficiency can be determined by comparison of the use of standards having the same radioelements and solids content as the test samples.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous effluents, and can be used for either absolute or relative determinations. It is sensitive to beta emissions above 0.1 MeV in energy and activity levels above 0.5 pCi/ml of liquid sample. Method does not measure those radioelements which are volatile under conditions of analysis.		
B) INTERFERENCES/LIMITATIONS High solids content in the sample as well as solids which are present between the test sample and the detector interfere. Excessive alpha, gamma, and X-ray emissions interfere, since most beta radiation counters can be used to measure these types of radiation as well.		
C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE The limit of sensitivity of both proportional and Geiger-Muller counters is related to background radioactivity. Both massive shielding and anti-coincidence detectors and circuitry can be used to minimize background detection.		
B) ACCURACY Not available at this time; accuracy is dependent upon the accuracy of the standard (data furnished by supplier), the measurement method, the number of nucleids present as well as the number of types of radiation energies present.		
C) PRECISION See reference of G. Friedlander and J.W. Kennedy (Ref. 521) for precision data.		
6. REAGENTS REQUIRED Reagent grade water, concentrated nitric acid.	7. EQUIPMENT REQUIRED Beta particle counter, sample dishes, Bunsen burner or oven (103 to 105°C), standard laboratory glassware.	
8. KEYWORD INDEX: Radioactivity, aqueous effluents, proportional counter, Geiger-Muller counter, beta radiation.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-34, 02-02-01-36.		
10. REFERENCES		
A) PRIMARY SOURCE		
024	ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D 1890-66, "Standard Method of Test for Beta Particle Radioactivity of Water," American Society for Testing and Materials, Philadelphia, PA., 1971, pp. 465-472.	
204	Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 302, p. 598.	
B) BACKGROUND INFORMATION		
521	Friedlander, G., and J.W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N.Y., 1955.	
517	Goldin, A.S., J.S. Nader and L.R. Setter, "The Detectability of Low-Level Radioactivity in Water," J. Am. Water Works Assoc., 45, 73 (1953).	
520	Heath, R.L., "Scintillation Spectrometry, Gamma Ray Spectrum IDO 16880," Technical Information Division, U.S. Atomic Energy Commission, Washington, D.C., Vols. 1 and 2, 1964.	
519	National Center for Radiological Health, "Radioassay Procedures for Environmental Samples," PHS Publ. No. 999-RH-27, U.S. Dept. of Health, Education and Welfare, Washington, D.C., Jan. 1967.	

1. TITLE METHOD FOR DETERMINATION OF ALPHA AND BETA RADIOACTIVITY COUNTING ERROR	2. IDENTIFICATION CODE 02-02-01-38
3. ABSTRACT OF METHODOLOGY	
Counting error, E (in picocuries/sample), at the 95% confidence level is calculated using Eq. 1: $E = \frac{1.96 \sigma(R)}{2.22 \epsilon} \quad (1)$ where $\sigma(R)$ is the standard deviation of the counting rate, and ϵ is counter efficiency. The term $\sigma(R)$ can be calculated using Eq. 2: $\sigma(R) = \left(\frac{R_0}{t_1} + \frac{B}{t_2} \right)^{1/2} \quad (2)$ where R_0 is the counting rate of the sample plus background, B is the background counting rate, and t_1, t_2 are the times in minutes in which the gross sample and the background counting rates were measured. Counter efficiency, ϵ, is determined as the result of plots of measurements of different weights of a known standard as a calibration curve. Counting error in picocuries/liter should be divided by sample volume in liters to give error in pCi/liter.	
4. APPLICATION: Compliance, engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to samples analyzed for total alpha radioactivity using proportional or scintillation counters (see 02-02-01-39) and for total beta radioactivity using proportional or Geiger-Muller counters (see 02-02-01-40). B) INTERFERENCES/LIMITATIONS N/A C) RECOMMENDED USE AREA Compliance testing.	
5. OPERATIONAL PARAMETERS	
A) RANGE See 02-02-01-39 and 40. B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED N/A
8. KEYWORD INDEX: Counting error, aqueous effluents, radioactivity, scintillation counter, proportional counter, alpha radiation, beta radiation.	
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-34, 02-02-01-35.	
10. REFERENCES	
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation. Washington, D.C., 1971, Method 302, 300C and F. B) BACKGROUND INFORMATION 522 Jarrett, A.A., "Statistical Methods Used in the Measurement of Radioactivity (Some Useful Graphs)," U.S. Atomic Energy Commission Document No. AFCU-262, Atomic Energy Commission, Washington, D.C., June 17, 1946. 523 Wader, J.S., G.R. Hagel and L.R. Satter, "Evaluating the Performance of the Internal Counter," <i>Nucleonics</i>, 12, 6, 29 (1954). C) FIELD APPLICATIONS	

1. TITLE METHOD FOR DETERMINATION OF RADIUM IN WATER		2. IDENTIFICATION CODE 02-02-01-37
3. ABSTRACT OF METHODOLOGY		
Method involves coprecipitation of total radium (radium-223, -224, and -226) with barium and lead sulfates. The precipitate is dissolved in ammoniacal EDTA, and the barium and radium sulfates are reprecipitated by treatment with acetic acid. The precipitate is collected, dried, and the alpha-radiation count determined using a proportional counter or scintillation counter (see 02-02-01-39). Method may be used for absolute measurements when the counter is calibrated with a standard such as radium-226, or for relative measurements by the comparison of samples with each other.		
4. APPLICATION: Compliance.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous effluents. B) INTERFERENCES/LIMITATIONS Excessive barium content (>0.2 mg) interferes in the determination of chemical yield. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is applicable to all sample sizes by making suitable reductions in sample size; the lower limit of sensitivity is one pCi/liter. B) ACCURACY N/A C) PRECISION N/A		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Reagent water, barium nitrate, lead nitrate, citric acid, ammonium hydroxide, disodium ethylenediamine tetra-acetate, methyl orange indicator, sulfuric acid.	Sample mounting discs or dishes, scintillation or proportional detector and scaler, Bunsen burner or oven (103 to 105°C), standard laboratory glassware.	
8. KEYWORD INDEX: Radium, aqueous effluents, proportional counter, scintillation counter.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-34, 02-02-01-36.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association and Water Pollution Control Federation, Washington, D.C., 1971, Method 304, p. 611. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analyses," 1971 Annual Book of ASTM Standards, Part 23, 02460-70, "Standard Method of Test for Radionuclides of Radium in Water," American Society for Testing and Materials, Philadelphia, PA., 1971, pp. 659-663. B) BACKGROUND INFORMATION 517 Goldin, A.S., "Determination of Dissolved Radium," <i>Anal. Chem. ANCHA</i>, 33, 406 (1961). 524 Halback, P.F. (ed.), "Radionuclide Analyses of Environmental Samples, Method RC-88A," U.S. Public Health Service Report R59-6, 1959. 525 Hallden, N.A., and J.H. Harley, "An Improved Alphacounting Technique," <i>Anal. Chem.</i>, 32, 1961 (1960). 526 Petrow, H.G., and R.J. Allen, "Estimation of the Isotopic Composition of Separated Radium Samples," <i>Anal. Chem. ANCHA</i>, 33, 1303 (1961).		

1. TITLE INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY	2. IDENTIFICATION CODE 02-02-02-01
3. ABSTRACT OF METHODOLOGY Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) is based on the observation of atomic emission spectra when samples in the form of an aerosol are injected into an inductively coupled plasma atomization and excitation source. The apparatus employed is essentially a flame emission technique, except that the flame is a plasma torch whose temperature is on the order of 7000°K. Figure 02-02-02-01A is a generalized schematic of the ICPOES system. In practice, the solutions to be analyzed are sprayed from a glass and Teflon nebulizer which aspirates approximately 3 ml per minute of solution with an argon flow rate of about 1 ml per minute. The plasma torch sits on a Rowland circle and the emitted light is dispersed by a curved grating along the curvature of the circle at specific points, depending on the emitted wavelength. Current commercial instrumentation employs up to 40 collection points (photomultipliers), so that 40 elements can be measured simultaneously.	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE ICPOES normally analyzes a sample after it has been placed in solution. Recent advances, however, make analysis of solid samples and gases possible. For routine analyses, the manufacturers recommend that the solutions contain less than 0.5% solids, but up to 1% solids can be tolerated. All elements can be analyzed using ICPOES, but the commercial instruments today are capable of measuring only 40 elements simultaneously. Since the collection points for the individual elements must be physically placed on the Rowland circle, they cannot be changed very readily. Consequently, it is important to either find an instrument employed by a commercial testing laboratory that has the elements of interest, or when purchasing an instrument, to select the elements carefully to provide the needed coverage for specific analysis needs. B) INTERFERENCES/LIMITATIONS While the high temperature of the plasma eliminates most matrix problems, there still exists a small degree of chemical interferences. Solids still must be reduced to solutions and the solids content of the solutions must be below 1%. This can cause problems when sodium carbonate fusion or sodium borate fusion is used as the dissolution technique. C) RECOMMENDED USE AREA This method is the recommended engineering evaluation R&D multi-element technique.	
5. OPERATIONAL PARAMETERS A) RANGE Powers of detection range from nanogram to fractions of micrograms per ml up through 4-5 orders of magnitude sensitivity. Table 02-02-02-01A gives the sensitivity for representative elements. B) ACCURACY For the major components of a sample, the accuracy ranges from 1-2%. For the lower limits of detection (ppm range) the accuracy is typically $\pm 15\%$. C) PRECISION The overall precision of the technique ranges from 5-10%.	
6. REAGENTS REQUIRED High purity water, argon gas.	7. EQUIPMENT REQUIRED Currently 2 companies are manufacturing ICPOES equipments: ARL in Sunland, California, and Jarrell Ash in Pittsburgh, Pennsylvania.
8. KEYWORD INDEX: Analyses, multi-element analyses, ICPOES.	
9. CROSS REFERENCE ID NUMBERS 02-02-01.	
10. REFERENCES A) PRIMARY SOURCE 234 Fassel, V.A., and R.N. Kniseley, "Inductively Coupled Plasma Optical Emissions Spectroscopy", <u>Anal. Chem.</u>, 46, 1110A (1974). B) BACKGROUND INFORMATION 235 Jones, J.L., R.L. Dahlquist, R.E. Hagt and J.W. Knoll, "Liquids Analysis with the Inductively Coupled Plasma Torch - a Multi-Channel Optical Emission System," Pittsburgh Conference, Cleveland, Ohio, 1974. C) FIELD APPLICATIONS 236 Dahlquist, R.L., R.E. Hoyt and J.W. Knoll, "Application of the Inductively Coupled Plasma Using Thermal and Direct Aerosol Generation," presented at the 21st Canadian Spectroscopic Symposium, Ottawa, Ontario, Canada, October 7-9, 1974.	

TITLE INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY
(CONTINUED)

ID NO. 02-02-02-01

Table 02-02-02-01A. Limits of Detection Determined with the Induction Coupled Plasma Under a Single Set of Conditions (Aqueous Solutions).*

Element	Height of Observation Above Coil (mm)	2 σ Limit of Detection ($\mu\text{g/ml}$)
Ag 3280	16.5	0.01
As 1937	16.5	0.04
B 2498	16.5	0.03
Cd 2265	16.5	0.02
Cr 2835	16.5	0.006
Cr 2677	16.5	0.007
Cu 3247	16.5	0.003
Fe 2599	16.5	0.003
Mg 2795	16.5	0.0002
Mn 2576	16.5	0.003
Mo 3170	16.5	0.06
Na 3302	16.5	1.8
Ni 2316	16.5	0.04
Pb 2203	16.5	0.05
Sb 2068	16.5	0.07
Se 1960	16.5	0.08
Sn 1899	16.5	0.05
Ta 2400	16.5	0.02
V 3110	16.5	0.005
Zn 2138	16.5	0.009

* From Reference 234

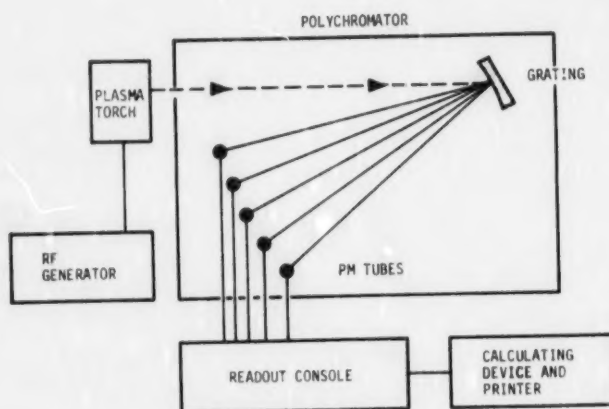


Figure 02-02-02-01A. Block Diagram of Plasma Torch and Spectrometer.

1. TITLE X-RAY FLUORESCENCE OF ENVIRONMENTAL SAMPLES		2. IDENTIFICATION CODE 02-02-02-02
3. ABSTRACT OF METHODOLOGY		
X-ray fluorescence (XRF) is based on the measurement of secondary X-rays that are produced when a sample is irradiated with a beam of X-rays. In order to perform the most accurate analysis, the analyst must be aware of several factors: 1. Sample preparation: XRF can be used to directly measure particulates collected on filter material, but other environmental samples (solids and liquids) can be analyzed by XRF. Figure 02-02-02-02A (from Gould) summarizes sample preparation techniques. Birks or Morrison can provide more specific information. (See References below.) 2. Standards: In general, standards should match as closely as possible the sample to be analyzed, otherwise correction factors for matrix effects will be required. Typical standard preparation consists of evaporating a solution of salts on filter paper or addition of internal standards to solutions or to a borate glass fusion. Recently, standard metal particulates were generated and collected on a filter media to provide standards (Dharmajan). 3. Filter Material: To obtain accurate and sensitive analyses of particulates collected on filter media, the background impurities must be low. Birks (EPA-R2-72-063) has shown Millipore or Whatman filter paper to be the best choices for XRF analysis. Glassfiber can be used if one of comparable purity can be found. 4. Particle Size Effects: The larger the particle, the greater the decrease in sensitivity for the same $\mu\text{g}/\text{cm}^2$ concentration. For particles above a few microns the X-ray intensity falls off dramatically. Empirical or theoretical calculations to correct for this problem can be difficult or impossible on environmental samples. Use of fractionating impactor reduces this problem by providing standard-sized samples which can be corrected on an individual basis. 5. Matrix Effects: Problems are encountered especially with the light elements due to absorption of low energy secondary X-rays by the filter material or aerosol particles. In particular, one must be aware that variations in the elemental compositions within a particle will affect the observed intensity by changing the degree of absorption. 6. Resolution: XRF energy dispersive instruments (XRF-ED) are relatively inexpensive and faster than crystal spectrophotometers (XRF-CS). However, XRF-ED cannot separate the K line of one element from the K line of the next lower atomic number in the region of S to Ni. For this reason (and sensitivity considerations) it is necessary to use XRF-CS to separate the lines of interest and retain reasonable counting times for low concentrations.		
4. APPLICATION: Engineering evaluation R&D		
A) OPERATIONAL SCOPE This method can be used on liquid or solid samples from any industrial stream. This method is particularly useful for particulates collected on filters or impactor stages. B) INTERFERENCES/LIMITATIONS See Abstract of Methodology. C) RECOMMENDED USE AREA Analysis of collected particulates on filters for engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE See Table 02-02-02-02A for sensitivities. Ppm to percentage composition. B) ACCURACY Variable, depends on sample, element and standards. Estimated at $\pm 25\%$ for environmental samples. (see Abstract of Methodology) C) PRECISION $\pm 5\%$		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Reagents required will depend on preparation technique employed, but in theory and practice samples can be run directly.		XRF either with a crystal spectrometer for high resolution at low sensitivities or with energy dispersive detector for less complex, higher concentration samples.
8. KEYWORD INDEX: Analysis, XRF.		
9. CROSS REFERENCE ID NUMBERS 02-01-02, 02-01-03.		
10. REFERENCES		
A) PRIMARY SOURCE 237 Birks, L.S., "X-ray Spectrochemical Analysis," Interscience Publishers, New York, 1969. B) BACKGROUND INFORMATION Refer to Continuation Sheet. C) FIELD APPLICATIONS Refer to Continuation Sheet.		

TITLE X-RAY FLUORESCENCE OF ENVIRONMENTAL SAMPLES (CONTINUED)

ID NO. 02-02-02-02

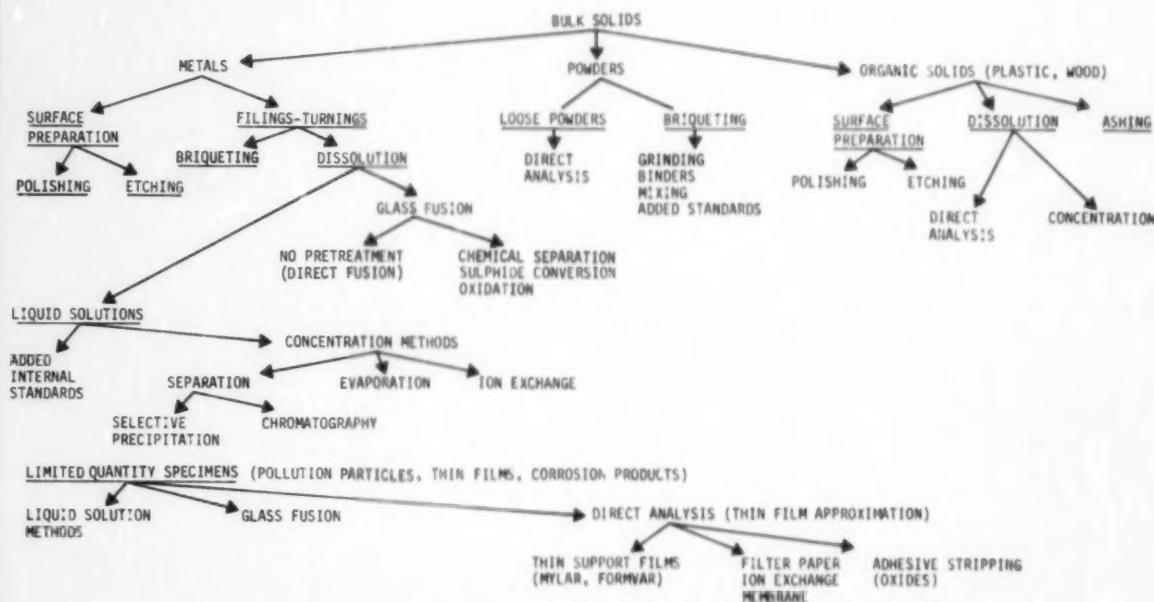
10. REFERENCES (Cont)

B) BACKGROUND INFORMATION

- 166 Morrison, G.H. (ed.), "Trace Analysis Physical Needs," Interscience Publishers, New York, N. Y., 1965.
- 238 Gould, R.W., "Recent Developments in Wavelength Dispersive X-ray Spectrometric Analysis," *Am. Lab.*, 12 (July 1974).
- 239 Gelfrich, J.V., L.S. Birks and P.G. Burkhalter, "X-ray Spectrometry for Particulate Air Pollution - A Quantitative Comparison of Techniques," *Anal. Chem.*, 45, 2002 (1973).
- 240 "Dhanmarjan, V., and P.W. West, "A Precise Method for the Generation of Standard Metal Salt Particles," *Anal. Chim. Acta*, 69, 43 (1974).
- 241 Birks, L.S., P.G. Burkhalter and J.V. Gelfrich, "Development of X-ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions," Phase II: Evaluation of Commercial Multiple Crystal Spectrometer Instruments," Naval Research Laboratory, Washington, D. C., EPA Report No. R2-72-063, November 1972.
- 242 Birks, L.S., and J.V. Gelfrich, "Development of X-ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions," Phase II: Evaluation of Commercial Multiple Crystal Spectrometer Instruments," Naval Research Laboratory, Washington, D. C., NRL Report 7617, June 1973.
- 243 Jakleric, J.M., et al., "Application of X-ray Fluorescence Techniques to Measure Elemental Composition of Particles in the Atmosphere" in "Analytical Methods Applied to Air Pollution Measurement" edited by R.K. Stevens and W.F. Hargett, Ann Arbor Science, Ann Arbor, Michigan, 1974.

C) FIELD APPLICATIONS

- 244 Bowman, H.R., F. Asaro and J.G. Conway, *Environ. Sci. Tech.*, 6, 558 (1972).
- 245 Gianque, R.D., H.E. Brown and L.Y. Goda, "Characterization of Aerosols in California by X-ray Induced X-ray Fluorescence Analysis," *Environ. Sci. Tech.*, 8(5), 436 (1974).

Figure 02-02-02A. From *Am. Lab.*, 12 (July 1974).

TITLE X-RAY FLUORESCENCE OF ENVIRONMENTAL SAMPLES (CONTINUED)

ID NO. 02-02-02-02

Table 02-02-02-02A. From *Anal. Chem.*, 45, 2002 (1973).100-Second Detection Limits ^{a)} for Various X-Ray Techniques, ng/cm²

	Al	S	K	Ca	V	Fe	Cu	Zn	Se	Br	Zr	Au	Pb
WAVELENGTH DISPERSION													
X-Ray tube excitation													
As measured													
(900 watts)													
Cr tube	360	52	3	10	53	150	160	180	820	390			1000
Rh tube	85	13	18	29	33	30	49	51	150	210			260
W tube		52			29	36	40		100	160			
ENERGY DISPERSION													
X-Ray tube excitation													
As measured													
(150 watts ^{b)})													
Mo tube				350	160	120		100	48				110
W tube				33	34	39		160	110				190
W tube-Ni foil		570	220	140	90	120		110	81				110

a) Detection limit defined as 3 σ of background for given time.

b) 0.002 steradian aperture between X-ray tube and sample.

1. TITLE OPTICAL EMISSION SPECTROSCOPY (DC ARC/AC SPARK)	2. IDENTIFICATION CODE 02-02-02-03
3. ABSTRACT OF METHODOLOGY Optical Emission Spectroscopy (OES) pertains to emission spectra in the near UV, visible, or near IR wavelength regions of the electromagnetic spectrum. Most direct trace element analysis by OES involves the use of the DC arc. The sample in a graphite electrode is first made positive; then, a current of up to 30 amps (depending on the electrode diameter) is passed through the sample. The resultant light emissions are characteristic of the elements present. A recent improvement to the DC arc method is the Stallwood Jet. This device stabilizes the arc, reduces background and selective volatilization, and increases signal. The DC arc is employed both for trace and microanalysis, but is less suited for the latter, since the intense heat generated frequently results in erratic sample vaporization. The AC spark method, in which two graphite electrodes bearing the sample are sparked together at a small (2 mm) gap with low capacitance and high inductance for cool excitation, is more suitable for microanalysis. Liquid samples can be determined by means of a liquid sample injection system. In one method (porous cup method), the sample is contained in a "cup" made of nonporous carbon. When arcing commences, the cup is broken and the sample then comes in contact with the carbon counter electrode positioned beneath it. In a second (direct) method, the liquid sample is placed on a solid matrix and loaded into a cup. Suitable matrix solids include SiO_2, MgO and carbon. The sample-bearing matrix must be packed tightly in the cup to ensure that it will remain positioned during arcing. OES is somewhat less costly than SSMS techniques, although sensitivities on the order of tens of nanograms rather than tenths of nanograms can only be achieved.	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE OES is applicable to bulk solids, powders and liquids; OES is not suited to the determination of gases, halogens, carbon, sulfur, phosphorous, and selenium. DC arc is useful for trace element analysis; AC spark is suitable for microanalysis. B) INTERFERENCES/LIMITATIONS Organic materials tend to ignite in the DC arc and must be removed prior to analysis (see 02-01-04-03). Arc wandering causes wild fluctuations in radiation emitted; these effects of arc wandering are mitigated by using narrow (1/8 in. or 0.32 cm) diameter electrodes and current adjustment. C) RECOMMENDED USE AREA This is an alternate recommended to engineering evaluation R&D procedure for trace element analysis and microanalysis using OES for solids (bulk, ash), and liquids.	
5. OPERATIONAL PARAMETERS (See reverse side) A) RANGE B) ACCURACY C) PRECISION	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED DC arc or AC spark unit (Pacific Spectrochemical Co., Los Angeles), including prisms and/or diffraction gratings, mirrors, slits; and detection apparatus (e.g., photographic plate); development equipment.
8. KEYWORD INDEX: Optical emission spectrometry, DC arc/AC spark, solid samples, liquids, multi-element analysis.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01; 01-03; 01-04; 01-06.	
10. REFERENCES (See reverse side) A) PRIMARY SOURCE B) BACKGROUND INFORMATION C) FIELD APPLICATIONS	

TITLE OPTICAL EMISSION SPECTROSCOPY (DC ARC/AC SPARK) (CONTINUED)

ID NO. 02-02-02-03

5. OPERATIONAL PARAMETERS

- A) RANGE** With a range of 1650-9000 Å, OES can be used to determine over 70 elements simultaneously; sample sizes of over 1g to 10^{-9} g can be determined. See Table 02-02-02-03A for persistent lines and sensitivities of the elements using DC arc method (with and without Stallwood jet).
- B) ACCURACY** ~30 - 50% accuracy.
- C) PRECISION** Precision varies, depending on instrumentation used. DC arc technique has lower reproducibility (higher sensitivity) than AC spark method. The Stallwood jet improves the precision and accuracy achieved using the open arc approach.

10. REFERENCES**A) PRIMARY SOURCE**

- 166 Morrison, G.H. (ed.), "Trace Analysis Physical Methods," Interscience Publishers, New York, N. Y., 1965, Chapter 6.
- 246 ASTM Committees A-6, B-4 and F-1, "Magnetic Properties," 1971 Annual Book of ASTM Standards, Part 8, "Standard Method for Spectrochemical Analysis of Emissive Carbonates by the Powder DC Arc Technique," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 748.

B) BACKGROUND INFORMATION

- 247 "Sampling and Analytical Strategy for Potentially Hazardous Compounds in Petroleum Refinery Streams," Radian Corporation, Austin, Texas, p. 50.
- 248 Brown, R.M., et al, Amer. Lab., 4(11), 29 (1972).
- 249 Fred, M., W.H. Nachtrieb and F.S. Tompkins, J. Opt. Soc. Am., 37, 279 (1947).
- 250 Morris, J.M., and F.X. Pink, ASTM Spec. Tech. Pub., No. 221, 1957.

C) FIELD APPLICATIONS

- 251 Augey, H., J. Opt. Soc. Am., 39, 292 (1949).
- 252 Churchill, W.L., and A.H.C.P. Gillieson, Spectrochim. Acta., 5, 238 (1952).
- 154 Seeley, J.L., and R.K. Skogerboe, "Combined Sampling and Analysis Method for the Determination of Trace Elements in Atmospheric Particles," Anal. Chem., 46(3), 415, 1974.

TITLE OPTICAL EMISSION SPECTROSCOPY (DC ARC/AC SPARK) (CONTINUED)

ID NO. 02-02-02-03

Table 02-02-02-03A. (1) Persistent Lines and Sensitivities of the Elements^a

Element	Line, A.	Limit of detection, ppm		Element	Line, A.	Limit of detection, ppm	
		Open Arc	Stallwood Jet			Open Arc	Stallwood Jet
Ag	3280.7	1	0.5	Mn	2576.1	5	1
Al	3092.7	10	5	Na	3302.3	500	500
As	2349.8	100	50	Nb	3094.2	10	5
Au	2428.0	<5	<5	Nd	4303.5	20	5
B	2497.7	2	2	Ni	3414.8	20	5
Ba	4554.0	5	2	P	2535.7	100	50
Be	2348.6	0.1	0.5	Pb	2833.0	20	5
	3130.4	0.5	0.02	Pd	3242.7	10	5
Bi	3067.7	5	2	Pr	4225.3	20	5
Ca	4226.7	1	0.2	Pt	3064.7	<5	<5
Cd	3261.1	20	10	Rb	4201.8	>1000	1000
Ce	4186.6	1000	500	Re	3460.5	50	10
Ce ^a	4186.6	10	5	Rh	3434.9	10	<5
Co	3453.5	20	5	Ru	3436.7	100	10
Cr	2835.6	10	5	Sb	2598.0	50	50
Cs	4555.4	500	500	Sc	4023.7	1	0.5
Cu	3247.5	1	0.5	Se	2062.8	1000	500
Dy	4046.0	5	2	Si	2881.6	1	0.5
Er	3692.6	5	2	Sm	4424.3	20	5
Eu	4594.0	5	2	Sn	3175.0	20	5
Fe	3020.6	5	2	Sr	4077.7	50	5
Ga	4172.1	20	5	Ta	3311.2	—	—
Ga	2943.6	5	5	Tb	3509.2	50	10
Gd	3422.5	10	2	Te	2385.8	500	100
Ge	2651.2	5	5	Th	4019.1	500	500
Hf	3194.2	50	10	Ti	3349.0	10	1
Hg	2536.5	500	50	Tl	3775.7	50	20
Ho	3891.0	5	2	Tm	3462.2	5	2
In	4101.8	20	5	U	4241.7	500	500
In	3256.1	10	<5	V	3093.1	20	5
Ir	3220.8	50	10	W	4302.1	100	100
K	4044.1	>1000	1000	Y	3242.3	5	2
La	3949.1	5	2	Yb	3289.4	1	0.5
Li	3232.6	500	500	Zn	3302.6	50	10
Lu	2615.4	5	2	Zr	3496.2	50	10
Mg	2795.5	0.2	0.2				

(1) Cited in Morrison, G. H., "Trace Analysis: Physical Methods," New York, Interscience Publishers, 1965, p. 197.

^aThe data in Table 1 were obtained with a graphite matrix for all of the elements save the rare earths for which the matrix was lithium carbonate (Spex semiquantitative G and L Standards). A 3.4 m spectrograph with a 600 L/mm grating set for the first order was used.

2. IDENTIFICATION CODE

02-02-04

1. TITLE DIFFERENTIAL PULSE ANODIC STRIPPING OF TRACE METALS**3. ABSTRACT OF METHODOLOGY**

Anodic Stripping Voltammetry (ASV) is similar to classical polarographic analysis, but performs the analysis in two steps. Using a hanging mercury drop electrode (HMDE) or a thin film mercury electrode, a portion of the metals in the solution is preconcentrated by electrolytic deposition on the HMDE. The metals in the amalgam are reoxidized to the component ions by applying a differential pulse voltammetry waveform. This DC pulse waveform consists of a slow linear potential ramp upon which are superimposed fixed height voltage pulses. By sampling the current before and after the pulse, a second derivative of the classical polarographic waveform is measured, generating a sharp peak for each element.

Solids or particulates are dissolved prior to analysis (see 02-01-04) and placed into a suitable electrolyte. By varying deposition potential, electrolyte and complexing agents, interelement effects and background current can be minimized while peak separation and height are maximized.

4. APPLICATION: Engineering evaluation R&D.**A) OPERATIONAL SCOPE**

The main benefit of DPASV (differential pulsed ASV) is its extreme sensitivity to trace metals such as Cu, Zn, Cd, As, Sn, Se, and Pb. These metals have been determined in waste effluent, tap water, cooling water, and in solid matrices after a dissolution step.

Note: Because of DPASV's sensitivity, high purity reagents (see 02-01-01) must be used for the best results.

B) INTERFERENCES/LIMITATIONS

Formation of Zn-Cu or Ni-Zn intermetallics at the HMDE can be troublesome when they are present in high concentrations. Organics present in the sample matrix should be removed prior to analysis to avoid large background or spurious results.

C) RECOMMENDED USE AREA

Trace metal analysis of Pb, As, Se, Cd, Sn, Zn, and Cu for engineering evaluation R&D.

5. OPERATIONAL PARAMETERS

- A) RANGE 5 ppb to 10 ppm for Cd, Pb, Cu, Sn, Zn, 0.6 ppb to 60 ppb for As,
8 ppb to 400 ppb for Se.
B) ACCURACY N/Q ($\pm 20\%$ estimated).
C) PRECISION $\pm 5\%$

6. REAGENTS REQUIRED

Depends on element determined.

7. EQUIPMENT REQUIRED

A typical DPASV unit is made by Princeton Applied Research, Princeton, New Jersey. Model 374 is completely automated for continuous operation.

8. KEYWORD INDEX: Analysis, differential pulsed ASV.**9. CROSS REFERENCE ID NUMBERS** 02-01-04, 02-01-01.**10. REFERENCES****A) PRIMARY SOURCE**

- 253 Siegerman, H., and G. O'Dunn, "Differential Pulse Anodic Stripping of Trace Metals," Am. Lab., June 1972.

B) BACKGROUND INFORMATION

- 254 Barker, G.C., and A.W. Gardner, Z. Anal. Chem., **173**, 79 (1960).
255 Christian, G.D., "Anodic Stripping Pulse Voltammetry," J. Electroanal. Chem., **23**, 1 (1969).
256 "Conversion Procedures for Model 174 to Model 374," Princeton Applied Research Corp., Princeton, New Jersey, February 1976.

TITLE DIFFERENTIAL PULSE ANODIC STRIPPING OF TRACE METALS (CONTINUED)

ID NO. 02-02-02-04

C: FIELD APPLICATIONS

- 257 Colovas, G., J. Moyers and A.S. Wilson, Anal. Chem. Acta, 64(3), 457 (1973).
- 258 Myers, D.J., and J. Osteryoung, "Determination of Arsenic (III) at PPB Level by Differential Pulse Polarography," Anal. Chem., 45(2), 267 (1973).
- 259 Princeton Applied Research, "Selenium as Se-DAB Complex," Application Brief S-1, PAR, Princeton, New Jersey.
- 260 Griffin, D.A., Anal. Chem., 41, 462 (1969).
- 261 Princeton Applied Research, "Differential Pulse Stripping Analysis of Tap Water," Application Note 107, PAR, Princeton, New Jersey.

1. TITLE INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)		2. IDENTIFICATION CODE 02-02-02-05
3. ABSTRACT OF METHODOLOGY		
A sample of liquid, solid or particulates on a filter is exposed to a source of neutrons. The radioactive isotopes formed emit characteristic gamma rays which are monitored using a thallium activated sodium iodide or lithium drifted germanium detector. The gamma rays are absorbed by the Tl-NaI crystal and readmitted as light in the visible region. A photomultiplier monitors these flashes of light, while a multichannel analyzer converts this signal into an intensity versus energy spectrum. Calibration can be done directly from counting data using the appropriate correction factors in the literature, but in practice known quantities of the elements are also activated and compared to the sample values. Because of the extreme sensitivity of the method, care in collection and handling of the samples is important (see 02-01-02, 03).		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE This method can measure elements from Na to Hg in any sample with minimal sample preparation. B) INTERFERENCES/LIMITATIONS An important environmental element, Pb, cannot be measured by this method. Long periods of time for decay and chemical separations are sometimes necessary to remove interfering radioisotopes from complex matrices. This method is not readily available commercially. C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D survey method for multi-element analysis.		
5. OPERATIONAL PARAMETERS		
A) RANGE Elements from Na through Hg at ppb sensitivities (see Table 02-02-02-05A for exact values). B) ACCURACY ± 5 to $\pm 25\%$. C) PRECISION ± 5 to $\pm 25\%$.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
N/A	Commercial laboratories normally are employed to perform this analysis. For example: General Activation Analysis, 11575 Dorrento Rd. No. 214, San Diego, Ca. 92121.	
8. KEYWORD INDEX: Analysis, INAA.		
9. CROSS REFERENCE ID NUMBERS 02-01-02, 03.		
10. REFERENCES		
A) PRIMARY SOURCE 262 Desoete, D., R. Gijbels and J. Hoste "Neutron Activation Analysis," Wiley-Interscience Publishers, New York, 1972. B) BACKGROUND INFORMATION 263 Kay, M.A., M. Eichor, D. Gray, D. McKnown and J. Vogt, "Neutron Activation Analysis in Environmental Chemistry," <u>Am. Lab.</u>, <u>39</u> (July 1973). C) FIELD APPLICATIONS 264 Dams, R., A. Rahn and J.W. Winchester, <u>Environ. Sci. Tech.</u>, <u>6</u>, 441 (1972). 265 Des, H.A., J.P.M. Dyong and J.E. Evendijk, <u>J. Radioanal. Chem.</u>, <u>13</u>(2), 413 (1973). 265 Matousek, J.P., and K.G. Brodie, <u>Anal. Chem.</u>, <u>45</u>, 160 (1973).		

TITLE INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) (CONTINUED)

ID NO. 02-02-02-05

10. REFERENCES (Cont)

- 267 Iddings, F.A., *Environ. Sci. Tech.*, **3**, 132 (1969).
 268 Zeller, W.M., and G.E. Gordon, *Anal. Chem.*, **42**, 256 (1970).

Table 02-02-02-05A.

Neutron Activation Analysis Detection Limits^a
 (based on a 1-hr irradiation at
 $4.5 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$)^b

Atomic number	Element	Detection ^c limit, μg	Atomic number	Element	Detection ^c limit, μg
11	Na	0.0003	47	Ag	0.0003
12	Mg	0.01	48	Cd	0.0004
13	Al	0.0005	49	In	0.000003
14	Si	3.0	50	Sn	0.001
16	S	7.0	51	Sb	0.0002
17	Cl	0.003	52	Te	0.002
19	K	0.01	53	I	0.00001
20	Ca	0.1	55	Cs	0.00005
21	Sc	0.001	56	Ba	0.0003
22	Ti	0.004	57	La	0.0004
23	V	0.00004	58	Ce	0.01
24	Cr	0.05	59	Pr	0.002
25	Mn	0.000004	60	Nd	0.0006
26	Fe	10.0	62	Sm	0.00003
27	Co	0.0003	63	Eu	0.000003
28	Ni	0.02	64	Gd	0.0006
29	Cu	0.0001	65	Tb	0.003
30	Zn	0.008	66	Dy	0.000002
31	Ga	0.0001	67	Ho	0.00007
32	Ge	0.003	68	Er	0.0001
33	As	0.0002	69	Tm	0.03
34	Se	0.002	70	Yb	0.0005
35	Br	0.0001	71	Lu	0.00002
37	Rb	0.02	72	Hf	0.001
38	Sr	0.0001	73	Ta	0.05
39	Y	0.02	74	W	0.0002
40	Zr	0.1	75	Re	0.00006
42	Mo	0.005	77	Ir	0.00002
44	Ru	0.001	78	Pt	0.01
45	Rh	0.0001	79	Au	0.00001
46	Pd	0.002	80	Hg	0.01

^aFrom Kay, et al, *Am. Lab.*, **39** (July 1973).

^bOther experimental parameters: zero decay time, 7.5-cm-diam X 7.5-cm solid NaI (Tl) detector with 31% counting geometry, and 1.27-cm polystyrene beta absorber. Minimum detectable photopeak count rate taken as 100 cpm for $t_{1/2} < 1 \text{ hr}$ and 10 cpm for $t_{1/2} > 1 \text{ hr}$.

^cThe detection limits for many of these elements can be increased by increasing the irradiation time. On the other hand, some of these detection limits may be limited by blank values for the collection and irradiation containers.

2. IDENTIFICATION CODE

02-02-06

1. TITLE SPARK SOURCE MASS SPECTROMETRY (SSMS) WITH PHOTOGRAPHIC PLATE DETECTION

3. ABSTRACT OF METHODOLOGY

SSMS involves the breakdown of sample, which is present in the form of two electrodes, by an RF potential. The resultant ions are accelerated out of the source through electrostatic and electromagnetic analyzers, similar to organic mass spectrometry. The method of detection of the resultant ion beam determines the sensitivity and precision of the determination. Table 02-02-06A lists the absolute elemental detection limits of SSMS. There are two general types of SSMS detection systems: (a) photographic plate, and (b) electrical detection (02-02-07). The most widely used photoplate for SSMS ion detection is the Ilford Q2 photoplate. To achieve highest sensitivity, the attenuating plate exposure technique is used, whereby a series of exposure of the photoplate made using the sample are followed by a series of exposures on a reference sample. Doubly charged ions give approximately a factor-of-2 greater response than singly charged counterparts, which must be taken into account in final calculations. Precision and accuracy are highly dependent on spectral line widths and shapes. These parameters define optical densities, which are converted to ion densities by means of calibration curves. A number of computer-oriented systems for the derivation and integration of ion intensity profiles have been developed for use in accurate and precise determinations.

The photographic plate method is useful for the total characterization of a sample, since the entire periodic table is examined and possible interfering ions are resolved.

4. APPLICATION: Environmental assessment.

A) OPERATIONAL SCOPE

Method is applicable to the analysis of solid samples (coal, ash, particulates).

B) INTERFERENCES/LIMITATIONS

Emulsion variations may introduce significant error in measurement of line width. Highly reproducible plate development techniques must be employed in order to minimize errors.

C) RECOMMENDED USE AREA

This is the recommended environmental assessment procedure for multi-element analysis.

5. OPERATIONAL PARAMETERS

- A) **RANGE** Trace elements in quantities as small as 0.01 ppm can be determined. Particle sizes (coal) of 3 μ or less can be analyzed.
- B) **ACCURACY** Accuracy varies with method of data interpretation; accuracy typically ranges from 100-500. Analytical accuracies $\pm 15\%$ have been reported using computer-oriented methods for development of ion intensity profiles.
- C) **PRECISION** Precision varies with method of data acquisition. Precisions in the order of 10-20% have been reported using computer-assisted ion intensity profile methods.

6. REAGENTS REQUIRED

N/A

7. EQUIPMENT REQUIRED

Spark source mass spectrometer, such as Associated Electrical Industries Limited MS702R, with Q2 photographic plate.

8. KEYWORD INDEX: Spark source mass spectrometry (SSMS), photographic plate detection, solids, quantitative analysis.

9. CROSS REFERENCE ID NUMBERS 01-03-01-02, 01-03-02-01; 01-04-01-01; 01-06-01-01; 02-02-02-07.

10. REFERENCES

A) PRIMARY SOURCE

- 269 Ahearn, A.J., "Trace Analysis by Mass Spectrometry," New York, Academic Press, 1972, p. 9, 256, 484.
- 274 Nicholls, G.D., A. Graham, E. Williams and M. Wood, "Precision and Accuracy in Trace Element Analysis of Geological Materials Using Solid Source Spark Mass Spectrography," *Anal. Chem.*, **39**(6), 584 (1967).

B) BACKGROUND INFORMATION

- 270 Tranden, J., and K.O. Schery, *Anal. Chem.*, **225**, 295 (1967).
- 271 Owens, E.B., and N.A. Giardino, *Anal. Chem.*, **35**, 1172 (1963).
- 272 Kennicott, P.R., ASTM-E14 Conf. Mass Spectrom., p. 278 (1966).
- 276 Honig, R., in "Advances in Mass Spectrometry" (W.L. Mead, editor), Vol. 3, p. 101-129, Institute of Petroleum, London.
- 277 Cavad, A., R. Bourgillot and R. Stefoni, *C.R. Acad. Sci. Paris*, **B26**, 928 (1966).
- 278 Jarvorskil, J.F., "Sensitivity Calibration in Spark Source Mass Spectrometry," *Anal. Chem.*, **46**(14), 2080 (1974).
- 279 Sharkey, A.G., et al., "Advances in Coal Spectrometry; Mass Spectrometry," Bureau of Mines Report of Investigations #6318, 1963, 32 p.

TITLE SPARK SOURCE MASS SPECTROMETRY (SSMS) WITH PHOTOGRAPHIC PLATE
DETECTION (CONTINUED)

ID NO. 02-02-02-06

B) BACKGROUND INFORMATION (Continued)

- 189 ASTM Committee E-1 and E-2, et al., "General Test Methods," 1971 Annual Book of ASTM Standards, Part 30, E304-68, "Recommended Practice for Use and Evaluation of Mass Spectrometers for Mass Spectrochemical Analysis of Solids," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 916.

C) FIELD APPLICATIONS (continued)

- 280 Alvarez, R., D. Kelleher and P. Paulsen, "Simultaneous Determination of Trace Elements in Platinum by Isotope Dilution and Spark Source Mass Spectrometry," *Anal. Chem.*, **41**(7), 955 (1969).
- 281 "Analysis of Trace Elements in Coal by Spark Source Mass Spectrometry," Bureau of Mines Report of Investigations #7714, 1973, 8 p.
- 282 Kessler, T., et al., "Spark Source Mass Spectrometer Investigation of Coal Particles and Coal Ash," *Bu. Mines Tech. Prog. Rept.*, **42**, 1971, 15 p.
- 283 Ahearn, A.J., "Mass Spectrographic Detection of Impurities in Liquids," *Appl. Physics*, **32**(7), 1197 (1961).
- 284 Schmidt, F.A., O. Carlson, R. Conzenius and H. Svec, "Diffusion of Metallic Solutes in Vanadium Using Spark Source Mass Spectrometry as the Method of Analysis," *Anal. Chem.*, **46**(7), 810 (1974).
- 285 Hannay, N.B., and A.J. Ahearn, *Anal. Chem.*, **26**, 1056 (1954).

Table 02-02-02-06A. Absolute Detection Limits of Spark Source Mass Spectrometry⁽¹⁾, Ref. 269

Element	Detection Limit (nanograms)	Element	Detection Limit (nanograms)	Element	Detection Limit (nanograms)
Ar	0.03	Hf	0.4	Pu	-
Ag	0.2	Hg	0.6	Rb	0.1
Al	0.02	Ho	0.1	Re	0.2
As	0.06	I	0.1	Rh	0.09
Au	0.2	In	0.1	Ru	0.03
B	0.01	Ir	0.3	S	0.03
Ba	0.2	K	0.03	Sb	0.02
Be	0.008	Kr	0.1	Sc	0.04
Bi	0.2	La	0.1	Se	0.1
Br	0.1	Li	0.006	Si	0.03
C	0.01	Lu	0.1	Sm	0.5
Ca	0.03	Mg	0.03	Sn	0.3
Cd	0.3	Mn	0.05	Sr	0.09
Ce	0.1	Mo	0.3	Ta	0.2
Cl	0.04	N	0.01	Tb	0.1
Co	0.05	Na	0.02	Te	0.3
Cr	0.05	Ne	0.02	Th	0.2
Cs	0.1	Nb	0.08	Ti	0.05
Cu	0.08	Nd	0.4	Tl	0.2
Dy	0.5	Ni	0.07	Tm	0.1
Er	0.5	Np	-	U	0.2
Eu	0.2	O	0.01	V	0.04
F	0.02	Os	0.4	W	0.5
Fe	0.05	P	0.03	Xe	0.4
Ga	0.09	Pa	-	Y	0.07
Gd	0.5	Pb	0.3	Yb	0.5
Ge	0.2	Pd	0.3	Zn	0.1
H	0.0008	Pr	0.1	Zr	0.1
He	0.003	Pt	0.5		

(1) The absolute detection limits shown were calculated on the basis of experimental observations of Hannay and Ahearn, Ref. 285; detection limits from SSMS are usually listed as parts per million atomic.

1. TITLE MULTIELEMENT ANALYSIS USING SPARK SOURCE MASS SPECTROMETRY (SSMS) WITH ELECTRICAL DETECTION	2. IDENTIFICATION CODE 02-02-02-07
3. ABSTRACT OF METHODOLOGY The SSMS technique involves the ionization of the sample, which is mixed with graphite to form two electrodes, by applying an rf potential. The ions which are produced by the high voltage rf discharge (spark) are accelerated out of the source through electrostatic and electromagnetic analyzers similar to organic mass spectrometry. The method of detection of the resultant ion beam determines the precision and sensitivity of the determination. Electrical detection methods are more sensitive than photographic plate detectors. Problems in quantitative spectral interpretation due to line-width variations, which are present in photographic plate detection systems, are eliminated using electrical detection systems. Analyses are also considerably more rapid using electrical detection. Two types of electrical detection systems are available: Log ratio exponential scanning can be used in a rapid (9-10 minute) all-element survey analysis in which only moderate precision is required. Although slower, peak switching (electrostatic and magnetic) techniques allow greater statistical precision for up to 10 selected elements with very high sensitivity. Automatic spark discharge control has been developed for peak switching techniques, permitting unattended operation for long periods, as well as giving improved reproducibility. (See Table 02-02-02-06-A for the absolute detection limits of SSMS.)	
4. APPLICATION: Environmental assessment. A) OPERATIONAL SCOPE Method is applicable to the analysis of solid samples (coal, ash, particulates), and to detection of trace impurities in liquids with proper sample preparation (see reference 283). B) INTERFERENCES/LIMITATIONS Singly and doubly charged ions cannot be simultaneously determined, as with photoplate detection methods. Organic material must be removed prior to analysis. C) RECOMMENDED USE AREA This method can be used for environmental assessment.	
5. OPERATIONAL PARAMETERS A) RANGE Sensitivity of log ratio exponential scanning is 0.1 to 100 ppm, and is dependent upon multiplier gain. Sensitivity in the 1 to 5-nanogram range is attainable with electrostatic peak switching. B) ACCURACY Accuracy of the peak switching method is dependent upon the availability of standards. The absolute accuracy has been determined using standard steel samples; mean difference between observed and quoted values was 4.2% for impurities in the 500-2,500 ppm range. C) PRECISION (See reverse side)	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED Spark source mass spectrometer, such as the Associated Electrical Industries United MS207 R, with high gain electron multiplier (e.g., Allen Type 20-Stage), UV oscilloscope recorders, amplifiers, for log ratio exponential scanning; with integrator for peak switching.
8. KEYWORD INDEX: Spark source mass spectrometry; Log ratio exponential scanning; Electrostatic and magnetic peak switching; Electrical detection; Solids; Multielement analysis.	
9. CROSS REFERENCE ID NUMBERS 01-03-01-02; 01-04-02-01; 01-06-01-01; 02-02-02-06.	
10. REFERENCES A) PRIMARY SOURCE (See reverse side) B) BACKGROUND INFORMATION (See reverse side) C) FIELD APPLICATIONS (See reverse side)	

TITLE MULTIELEMENT ANALYSIS USING SPARK SOURCE MASS SPECTROMETRY (SSMS) WITH ELECTRICAL DETECTION (CONTINUED)

ID NO. 02-02-02-07

5. OPERATIONAL PARAMETERS (Continued)

C) PRECISION

Log ratio exponential scanning provides ± 20 -30% precision for concentrations in the 1 ppm atomic level. See Figure 02-02-02-07A for peak switching precisions based on data for impurities in copper; precision is typically $\pm 5\%$ at the submicrogram level for electrostatic peak switching; $\pm 2\%$ for chosen elements at 1 ppm concentrations.

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B) BACKGROUND INFORMATION

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C) FIELD APPLICATIONS

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Table of Contents for 02-03 Species Analysis

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02-03-02-26 Determination of Color by Spectrophotometric Method

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APPLICATION MATRIX FOR 02-03 SPECIES ANALYSIS

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
02-03-01-01	●		●
02-03-01-02	●		●
02-03-02-01	●		
02-03-02-02	●		●
02-03-02-03	●		●
02-03-02-04			●
02-03-02-05	●	●	
02-03-02-06			●
02-03-02-07	●	●	
02-03-02-08	●	●	
02-03-02-09	●	●	
02-03-02-10	●	●	
02-03-02-11	●	●	
02-03-02-12	●	●	
02-03-02-13	●	●	
02-03-02-14	●	●	
02-03-02-15	●	●	
02-03-02-16	●	●	
02-03-02-17	●	●	
02-03-02-18	●	●	
02-03-02-19			●
02-03-02-20	●	●	
02-03-02-21	●	●	
02-03-02-22	●	●	
02-03-02-23	●	●	
02-03-02-24	●	●	
02-03-02-25	●	●	
02-03-02-26	●	●	
02-03-02-27	●	●	
02-03-02-28	●	●	
02-03-02-29	●	●	
02-03-02-30		●	

SPECIES ANALYSIS ID No. 02-03

The abstracts in this section discuss two major categories: (02-03-01) laboratory gas analysis, and (02-03-02) anion analysis. The methods employed are gas chromatography, specific ion electrode, spectrophotometry, turbidimetry, gravimetric and titrimetric methods.

02-03-01 - Laboratory Gas Analysis - (Abstracts 02-03-01-01 to 02-03-01-02)

Laboratory analysis of gases, such as flue gases (02-03-01-01) and sulfur-containing gases (02-03-01-02), involves the use of gas chromatography (GC). Although GC is routinely used for qualitative and semi-quantitative analysis, with careful calibration quantitative measurements can be made.

Syringe, ampoule and valve techniques are the most widely used methods of introducing gaseous samples into the chromatogram. The use of pressure lock syringes is desirable in the analysis of gases since this method assures rapid injection of a precise quantity of pressurized sample. For the analysis of samples trapped in metal bombs, the bomb valve may be connected directly to the GC or to a sample reservoir by means of a simple valve connection. When the reservoir method is used, a supply of carrier gas is also connected to the reservoir by means of a separate valve. After the sample reservoir is initially filled with sample gas from the bomb, the bomb valve is closed off and the sample flushed into the chromatograph by opening the carrier gas valve.

Another important factor in the use of GC is the possibility of corrosion of the metal components of the GC lines and detection equipment by the reactive species (acid gases) in the trapped samples. This can be minimized by performing analyses on samples which are as small as possible, by flushing of the system after use with suitable inert gases, and by proper cleaning of exposed surfaces using standard cleaning techniques.

02-03-02 Anion Analysis (Abstracts 02-03-02-01 to 02-03-02-20)

Regarding the analysis of anions, modern methods involve use of specific ion electrodes, (02-03-02-01) spectrophotometry, gravimetric (02-03-02-04) and titrimetric methods (02-03-02-04, 06, 07-11, 17, 18). Ion concentrations

can be determined using specific ion electrodes in several different ways. When the direct measurement method is used, the concentration of the desired species is read directly from the scale of a specific ion meter or from a calibration curve. Matrix effects are an important consideration in direct determinations. In general, matrix interferences can be eliminated by the addition of small quantities of ionic strength or pH adjustors (acids, bases, buffers) to both standard and sample solutions prior to measurement.

When the approximate concentration of the sample is known, but a specific ion meter is not available, the preparation of a calibration curve can be eliminated by using the standard addition technique. This method involves original zeroing of the detecting meter with the electrodes immersed in the sample, followed by addition of a known volume of standardizing solution to the sample at a concentration approximately equal to the sample itself. The resulting change in potential is then measured, and the original sample concentration is determined by multiplying a Q value obtained from a "standard addition table" times the concentration of the standard solution.

Electrode titrations (02-03-02-01) greatly increase the number of species that can be measured. For example, T-type titrations, in which the electrode senses the level of titrant as it is added to the sample, have been applied to the determination of sulfate (lead titrant and electrode), aluminum (fluoride titrant and electrode) and EDTA (copper titrant and electrode). R-titrations, in which the electrode senses the reagent species that has been added to the sample before titration, extends the number of species that can be measured by electrode to include Ni, Zn, Mn and Sr.

Sample concentrations can be determined by incremental methods, which involve determination of the change in electrode potential when a standard solution is added to the sample (standard known addition) or when the sample is added to the standard solution (sample addition). The sample concentration can be determined using a reagent solution which precipitates, complexes, or reacts with the species being measured. Gram's plots, which are plots of series of incremental measurements, can be used to increase the sensitivity for many titrations.

Prior to sample measurement by SIE, some forms of sample preparation may be required. This may involve dissolution of the sample in appropriate solvent (or acid, base, buffer), adjustment of pH with standard buffer solutions, adjustment of ionic strength, or other methods to eliminate interferences. Many standard and commercial references are available which list recommended specific procedures for sample preparation (Reference 223).

Spectrophotometry is routinely used in quantitative determination of many anionic species (02-03-02, 02, 03, 05, 10, 12 through 16, 19, 20). The determinations are based on Beers' law, which states that successive increments in the number of identical absorbing molecules in the path of a beam of monochromatic radiation absorb equal fractions of radiant energy which traverses them. This law also indicates that the absorptivity of a species is a constant which is independent of concentration, path length and intensity of incident radiation. Since in many practical applications Beers' law is not rigorously obeyed, quantitative analyses are usually performed by means of calibration curves (plots of absorbance vs. concentration) using standard solutions.

Because of the extreme sensitivity of spectrophotometric measurements, care must be taken to prevent sample contamination by trace impurities. High purity water should be used in the preparation of reagents and samples. Excessive color due to species other than that being determined generally interfere with spectrophotometric analyses. Turbid solutions may require filtration in order to remove suspended solids.

Gravimetric and titrimetric procedures are routinely used in the analysis of anions such as Group VII elements, sulfate, and alkalinity (02-03-02-04, 06, 07-11, 17, 18). In order to obtain good accuracy and precision in gravimetric determinations, the actual precipitation should be carried out under controlled conditions. Factors such as temperature, period of digestion, number and type of washings prior to drying, etc., must be considered. Cleanliness of equipment and use of impurity-free water are important factors in gravimetric and titrimetric procedures. For high precision, titrations should be performed as far as possible under the same conditions, using the same equipment and personnel. For accurate results, blank determinations should accompany all sample determinations.

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- 223 Orion Research, "Analytical Methods Guide," 7th ed., Orion Research Incorporated, Cambridge, Mass., May 1975.

1. TITLE GC ANALYSIS OF FLUE GAS SAMPLES (INSTRUMENTAL ORSAT ANALYSIS)		2. IDENTIFICATION CODE 02-03-01-01
3. ABSTRACT OF METHODOLOGY		
Samples returned to the laboratory are analyzed on a GC employing a dual column (Porapak N and Molecular Sieve 5A), a gas sampling valve and a column switching valve to separate the components of a sulfur rich flue gas sample. While the switching operations can be manual, automatic valve switching is recommended. This system utilizes the "Series/Bypass" technique in which at selected times one column is bypassed by carrier gas flow, permitting certain components to be stored there while separations are made on the other column.		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE This method can be used to analyze sulfur rich flue gas stream for CO₂, ethylene, ethane, H₂S, O₂, N₂, CH₄, CO, H₂O, SO₂. B) INTERFERENCES/LIMITATIONS If a sample is obtained using grab sampling techniques (01-01-04), one must be aware that changes can occur in the sample. Analysis should be performed as soon as possible. On-line analysis requires a filtered particulate sample (02-05-01-01). C) RECOMMENDED USE AREA Engineering evaluation R&D at any combustion process.		
5. OPERATIONAL PARAMETERS		
A) RANGE This system will analyze flue gas components at their nominal concentration range. B) ACCURACY N/Q (±10% estimated). C) PRECISION N/Q (±10% estimated).		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
N/A	Dual column GC with FID & TC detector (Carle Instruments, Fullerton, California, makes a GC specifically for this application).	
8. KEYWORD INDEX:		
9. CROSS REFERENCE ID NUMBERS 01-01-04; 02-05-01-01.		
10. REFERENCES		
A) PRIMARY SOURCE 296 "Sulfur Rich Flue Gas Analysis," Application No. 153-C, Carle Instrument Co., Fullerton, California. B) BACKGROUND INFORMATION 297 Adams, D.F., et al, J.A.P.C.A., 15(1), 31 (1965). 298 Juvet, R.S., "Advances in Chromatography," Vol. 1, Marcel Dekker Inc., New York, 1966, p. 249. C) FIELD APPLICATIONS		

1. TITLE LABORATORY ANALYSIS OF SULFUR-CONTAINING GASES BY GC	2. IDENTIFICATION CODE 02-03-01-02
3. ABSTRACT OF METHODOLOGY The verification of sulfur-containing components from gas bomb and trap samples can be made by GC analysis with flame photometric detection having -30,000:1 specificity for sulfur and a reliable sensitivity of 1-10 ppb. Special columns are used, which contain deactivated silica gel, Tracor silica and/or Triton X. The chromatograph should be equipped with gas valve injection, dual columns, and temperature programming. Sample loop volumes may be determined based on anticipated concentrations of individual sample components. Generally, sample volumes of 0.25 to 0.5 ml are sufficient.	
4. APPLICATION: Environmental assessment, engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to flue gas, fugitive gas, etc., contained in bombs and other grab sample containers. (See 01-01-04-01, 01-01-04-02, 01-05-04-01, 01-05-04-02). Gases such as H₂S, SO₂ and CS₂ can be separated. B) INTERFERENCES/LIMITATIONS N/A C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment procedure for analysis of sulfur-containing gases by GC.	
5. OPERATIONAL PARAMETERS	
A) RANGE GC method has a sensitivity of up to 1-10 ppb for sulfur. B) ACCURACY ±5% or better. C) PRECISION ±10%	
6. REAGENTS REQUIRED Column packings cited above.	7. EQUIPMENT REQUIRED Standard GC apparatus, with flame photometer detector.
8. KEYWORD INDEX: Sulfur gas analysis, gas chromatography, flame photometric detection, silica gel (Tracor), Triton X.	
9. CROSS REFERENCE ID NUMBERS 01-01-04-01, 01-01-04-02; 01-05-04-01, 01-05-04-02.	
10. REFERENCES	
A) PRIMARY SOURCE 014 Hamersma, J.W., and S.R. Reynolds, "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," TRW Systems Group, EPA Contract No. 68-02-1412, March 1975, p. 5.11. B) BACKGROUND INFORMATION 299 "Operation Manual for MT150 Series Gas Chromatograph, Flame Photometric Detector and Nickel-63 High Temperature Electron Capture Detector," Tracor, Inc., Operations Manuals, 1968. C) FIELD APPLICATIONS 300 Adams, D.F., and R.K. Koppe, "Gas Chromatographic Analysis of Hydrogen Sulfide, Sulfur Dioxide, Mercaptans, and Alkyl Sulfide, and Disulfides," <u>Tappi</u>, 42(7), July 1959, p. 601-605.	

1. TITLE ANION ANALYSIS USING SPECIFIC ION ELECTRODE (SIE)		2. IDENTIFICATION CODE 02-03-02-01	
3. ABSTRACT OF METHODOLOGY			
Specific anion electrodes can be used to determine a wide variety of anions, including bromide chloride, cyanide, fluoride, iodide, nitrate, perchlorate, thiocyanate, etc. (See Table 02-02-01-18A.) For example, fluoride is determined potentiometrically using a selective ion fluoride electrode in conjunction with a standard junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale, or a selective ion electrode having a direct concentration scale for fluoride. (See 02-02-01-18 for titration procedures using SIE's.)			
4. APPLICATION: Environmental assessment.			
A) OPERATIONAL SCOPE Method is applicable to samples (aqueous samples, species absorbed in liquids) containing species such as bromide, chloride, etc. (See Table 02-02-01-018A.) B) INTERFERENCES/LIMITATIONS Extremes of pH may interfere. Cations which complex with specific anions may interfere in the analysis of the anion. C) RECOMMENDED USE AREA This is the recommended environmental assessment procedure for the determination of anions listed in Table 02-02-01-18A.			
5. OPERATIONAL PARAMETERS			
A) RANGE See Table 02-02-01-18A for detectable concentration ranges of specific anions. B) ACCURACY See continuation sheet. C) PRECISION See continuation sheet.			
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED	
pH adjustors and titrants; precipitation or complexing agents, when required.		Specific ion electrodes; specific ion meter or standard pH meter having an expanded millivolt scale; standard laboratory glassware (beakers, pipettes, volumetric flasks).	
8. KEYWORD INDEX: Specific ion electrodes, aqueous effluents, anions.			
9. CROSS REFERENCE ID NUMBERS 02-02-01-18; 01-02-02-01, 01-02-02-01; 01-05-01-02.			
10. REFERENCES			
A) PRIMARY SOURCE 223 Orion Research, "Analytical Methods Guide," Anion Research, Inc., 7th ed., May 1975. B) BACKGROUND INFORMATION See continuation sheet. C) FIELD APPLICATIONS See continuation sheet.			

TITLE ANION ANALYSIS USING SPECIFIC ION ELECTRODE (SIE) (CONTINUED)

ID NO. 02-03-02-01

5. OPERATIONAL PARAMETERS**B) ACCURACY**

Accuracy varies with the species being determined. For fluoride determination, a mean of 0.84 mg/l fluoride with a standard deviation of 0.03 was obtained using synthetic samples containing 0.85 mg/l fluoride by Analytical Reference Service, PHS.

C) PRECISION

± 0.03 for fluoride determination; see (b) above.

10. REFERENCES**B) BACKGROUND INFORMATION**

- 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA 625/6-74-003, Cincinnati, 1974, p. 65-7.
- 301 Ross, J.W., and M.S. Frant, "Potentiometric Titrations of Sulfate Using an Ion Selective Lead Electrode," Anal. Chem., **41**(7), 967 (1969).
- 302 Paletta, B., "The Direct Electrometric Measurement of Iodide and Iodate Ions," Mikrochim Acta, **6**, 1210 (1969).
- 303 Florence, T.M., "Differential Potentiometric Titration of Parts per Billion Chloride with Ion-Selective Electrodes," J. Electroanal. Chem., **31**, 77 (1971).

C) FIELD APPLICATIONS

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- 305 Langmuir, D., and R. Jacobson, "Specific-Ion Electrode Determination of Nitrate in Some Freshwater and Sewage Effluents," Envir. Sci. and Tech., **4**(10), 834 (1970).
- 306 Buck, M., and G. Ruesmann, "A New Semi-Automatic Method for Fluoride Determination in Plant and Air Samples," Fluoride, **4**(1), 5 (1971).
- 307 Driscoll, J.N., J.H. Becker, A.W. Berger, J.T. Funkhouser and J.R. Valentine, "Determination of Oxides of Nitrogen in Combustion Effluents with a Nitrate Ion Selective Electrode," paper presented at the 6th Annual Meeting of the Air Pollution Control. Assn., Atlantic City, N. J., June 1971.

TITLE ANION ANALYSIS USING SPECIFIC ION ELECTRODE (SIE) (CONTINUED)

ID NO. 62-03-02-01

Table 02-03-02-01A. Anion Analysis Using SIE.

Electrode	Type	Concentration Range (M)	Temperature Range (°C)	Interferences	Notes
bromide	solid-state	10^0 to 5×10^{-6}	0-80	max level: $S^{2-} \leq 10^{-7}$ M; $I^- < 2 \times 10^{-4}$ Br $^-$	
chloride	liquid	10^0 to 8×10^{-6}	0-50	max level * (M) $\left\{ \begin{array}{l} 6 \times 10^{-6} \text{ ClO}_4^-; \\ 8 \times 10^{-6} \text{ I}^-; 3 \times 10^{-5} \text{ NO}_3^-, \text{ SO}_4^{2-}; \\ 4 \times 10^{-5} \text{ Br}^-; 10^{-4} \text{ OH}^-; \\ 4 \times 10^{-4} \text{ OAc}^-, \text{ HCO}_3^-; \\ 7 \times 10^{-4} \text{ F}^- \end{array} \right.$ at 10^{-3} M Cl $^-$	
	solid-state	10^0 to 5×10^{-5}	0-80	$S^{2-} \leq 10^{-7}$ M; bromide, iodide, and cyanide may be present in trace amounts NO_3^- , SO_4^{2-} , HCO_3^- do not interfere	preferred for Cl $^-$ where possible
cupric	solid-state	saturated to 10^{-8}	0-80	max level: S^{2-} , Ag^+ , $\text{Hg}^{++} \leq 10^{-7}$ M; high levels of chloride, bromide, ferric, and cadmium interfere	can be used for chelometric indicator titrations for metal ions, e.g., Zn $^{++}$, Ni $^{++}$
cyanide	solid-state	10^{-2} to 10^{-6}	0-80	max level: $\left\{ \begin{array}{l} S^{2-} \leq 10^{-7}$ M; $I^- < 1/10$ CN $^-$; $\text{Br}^- < 5 \times 10^3$ CN $^-$; $\text{Cl}^- < 10^6$ CN $^-$ \end{array} \right.	electrode life limited at high cyanide concentrations
fluoride	solid-state combination	saturated to 10^{-6} saturated to 10^{-6}	0-80 0-80	max level: $\text{OH}^- < 0.1$ F $^-$	can be used to measure aluminum and phosphate by titration
iodide	solid-state	10^0 to 2×10^{-7}	0-80	max level: $S^{2-} < 10^{-7}$ M	can also be used to measure mercury
nitrate	solid-state	10^0 to 6×10^{-6}	0-50	max level * (M) $\left\{ \begin{array}{l} 10^{-7} \text{ ClO}_4^-; 10^{-5} \text{ I}^-; \\ 10^{-4} \text{ ClO}_3^-; 6 \times 10^{-4} \text{ Br}^-; \\ 4 \times 10^{-3} \text{ HS}^-; \\ \text{CN}^-, 2 \times 10^{-3} \text{ NO}_2^-; \\ 4 \times 10^{-2} \text{ HCO}_3^-, \text{ Cl}^-; \\ 10^{-1} \text{ OAc}^- \end{array} \right.$ at 10^{-3} M NO_3^-	Ag_2SO_4 may be added to samples with high chloride levels
perchlorate	liquid	10^0 to 2×10^{-6}	0-50	max level * (M) $\left\{ \begin{array}{l} 2 \times 10^{-3} \text{ I}^-; 5 \times 10^{-2} \text{ NO}_3^-; 4 \times 10^{-2} \text{ Br}^- \end{array} \right.$ at 10^{-3} M ClO_4^-	will directly measure periodate and permanganate
silver/sulfide	solid-state	10^0 to 10^{-7} Ag^+ or S^{2-}	0-80	max level: $\text{Hg}^{++} < 10^{-7}$ M	
thiocyanate	solid-state	10^0 to 5×10^{-6}	0-80	max level: $\text{OH}^- < \text{SCN}^-$; $\text{Br}^- < 0.003 \text{ SCN}^-$; $\text{Cl}^- < 20 \text{ SCN}^-$; $\text{NH}_3 < 0.13 \text{ SCN}^-$; $\text{S}_2\text{O}_3^{2-} < 0.01 \text{ SCN}^-$; $\text{CN}^- < 0.007 \text{ SCN}^-$; I^- , $S^{2-} < 10^{-7}$ M	

1. TITLE SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE WITH ALIZARIN COMPLEXONE REAGENT		2. IDENTIFICATION CODE 02-03-02-02
3. ABSTRACT OF METHODOLOGY Three ml of an acidic solution of lanthanum-alizarin buffered to 4.50 ± 0.02 is added to a 10 ml volumetric flask containing an aliquot of the sample, and diluted to the mark. The mixture is allowed to stand for 30 minutes and then the absorbance is measured at 622 nm in a 1 cm cell using a reagent blank as the reference. A calibration curve (prepared at the same temperature) is used to quantify the amount of F^- in the sample. Because of the possible interference from ions such as aluminum, iron, and phosphate, techniques such as distillation, diffusion or ion exchange must be employed to remove these interferences (see 02-01-01-01, 02).		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE This method can be used to analyze impingers, bubblers, and particulate matter (once it has been dissolved) for the fluoride content. By using a suitable separation procedure such as the Williard-Winter distillation technique, more complex solutions can be analyzed with this technique.		
B) INTERFERENCES/LIMITATIONS The lanthanum-alizarin complexone reagent has a pH sensitivity, so the solutions must not exceed the capacity of buffer system to maintain the apparent pH of 4.50 ± 0.02 . Aluminum and iron interfere with the fluoride reagent, and must be removed or the fluoride separated by distillation, diffusion or ion exchange.		
C) RECOMMENDED USE AREA This is the recommended environmental evaluation R&D procedure for F^- after the appropriate separation is used.		
5. OPERATIONAL PARAMETERS		
A) RANGE 0.002 to $1.40 \mu g$ of fluoride per ml. A lower detection range is available from 0.00 to $0.5 \mu g$ of fluoride per ml.		
B) ACCURACY N/Q		
C) PRECISION ± 0.015 to 0.025 micrograms of fluoride per ml.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Acetic acid, acetone, alizarin complexone, ammonium acetate ammonium hydroxide, lanthanum chloride, sodium fluoride.		Spectrophotometer, sample cells.
8. KEYWORD INDEX: Analysis, anion analysis, fluoride analysis.		
9. CROSS REFERENCE ID NUMBERS 02-01-01-01, 02.		
10. REFERENCES		
A) PRIMARY SOURCE 084 APHA, "Tentative Method of Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Methods)," No. 12202-01-68T, Washington, D. C., 1972.		
B) BACKGROUND INFORMATION 308 Belcher, R., and T. S. West, "A Comparative Study of Some Lanthanum Chelates of Alizarin Complexone as Reagents for Fluoride," <u>Talanta</u> , 8 , 863 (1961).		
C) FIELD APPLICATIONS		

1. TITLE BARIUM CHLORANILATE COLORIMETRIC SULFATE METHOD		2. IDENTIFICATION CODE 02-03-02-03
3. ABSTRACT OF METHODOLOGY The sulfate concentration in a liquid sample is determined by reaction with barium chloranilate in a pH controlled, 50% alcohol solution to yield the highly colored acid chloranilate. The concentration of the product colored species is determined spectrophotometrically at 530 nm. Since the barium chloranilate reacts 1 to 1 with sulfate in solution, the absorption is directly related to the sulfate concentration.		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE This method is primarily designed to provide an analytical finish for sampling method 01-01-03-01. This sulfate method can be applied to other liquid samples, but <u>extreme</u> precautions must be exercised because many cations and anions interfere with this method. (See Ref. 053 under background information for a detailed listing of interferences.)		
B) INTERFERENCES/LIMITATIONS Cations such as Al^{+3} , Ca^{+2} , Fe^{+3} , Pb^{+2} , Ca^{+2} , and Zn^{+2} cause interference through precipitation of the acid chloranilate ion. Anionic interferences such as oxalate and phosphate can interfere quite dramatically. Chloride and bicarbonate interfere, but to a much smaller extent. When this procedure is used in conjunction with 01-01-03-01, the glass wool filter will remove most of the particulates. Consequently, the possibility of interferences passing into the condenser or impinger system is low.		
C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D H_2SO_4 analytical finish (see 01-01-03-01).		
5. OPERATIONAL PARAMETERS		
A) RANGE 0 to 500 ppm sulfate		
B) ACCURACY N/Q		
C) PRECISION $\pm 0.4\%$		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Sodium carbonate, barium chloranilate, pH 5.6 buffer solution (acetic acid and sodium acetate), ethyl alcohol, hydrochloric acid, sulfuric acid.		Centrifuge, balance (mg.), spectrophotometer.
8. KEYWORD INDEX: Analysis, sulfate analysis, barium chloranilate.		
9. CROSS REFERENCE ID NUMBERS 01-01-03-01.		
10. REFERENCES		
A) PRIMARY SOURCE 053 ASTM, "Tentative Method of Tests for Sulfur Oxides in Flue Gases (Barium Chloranilate Controlled Condensation Method)," 1974 Annual Book of ASTM Standards, Part 26, Method D3226-73T, ASTM Standards, p. 700.		
B) BACKGROUND INFORMATION 309 Bertolacini, R.J., and J.E. Barney, <u>Anal. Chem.</u> , 29 , 281 (1957). 310 Carlson, R.M., R.A. Rosell and W. Vallejos, <u>Anal. Chem.</u> , 39 , 689 (1967).		
C) FIELD APPLICATIONS 311 Bertolacini, R.J., and J.E. Barney, <u>Anal. Chem.</u> , 30 , 202 (1958).		

1. TITLE GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF SULFATE SULFUR, PYRITIC SULFUR AND ORGANIC SULFUR IN COAL	2. IDENTIFICATION CODE 02-03-02-04
3. ABSTRACT OF METHODOLOGY Sulfate sulfur is determined by extracting a weighed sample of air-dried coal (ground to pass a No. 60 mesh sieve) with dilute hydrochloric acid, followed by precipitation with ammonium hydroxide, with subsequent precipitation with barium chloride and weighing as barium sulfate. (See 01-03-01-02 and 02-01-03-02 for sample collection and preparation procedures.) Pyritic sulfur is determined by extracting a weighed sample of coal with dilute nitric acid, followed by titrimetric determination of iron in the extract as a measure of pyritic sulfur. Pyritic sulfur is thus determined indirectly by measuring the amount of pyritic iron in the nitric acid extract. The pyritic iron in the extract is precipitated as the ferric hydroxide by adding ammonium hydroxide. The amount of iron present, which is equivalent to the amount of pyritic sulfur, is then determined by titration with potassium dichromate or permanganate. Organic sulfur is determined by subtracting the sum of the sulfate sulfur and pyritic sulfur from the total sulfur (See Reference 057).	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE The method is applicable to all sampled coals (ground to pass a No. 60 mesh sieve). B) INTERFERENCES/LIMITATIONS N/Q C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D procedure for the determination of sulfate sulfur, pyritic sulfur, and organic sulfur in coal.	
5. OPERATIONAL PARAMETERS A) RANGE Methods have sensitivities of ± 0.10 percent or less. B) ACCURACY 10% or better. C) PRECISION Permissible differences in results obtained in the same (different) laboratory include: Sulfate sulfur: 0.02 (0.04); pyritic sulfur, under 2 percent: 0.05 (0.03); pyritic sulfur, 2 percent or more: 0.10 (0.40).	
6. REAGENTS REQUIRED Reagent water; ammonium chloride, ammonium hydroxide, barium chloride, diphenylamine sulfonate indicator solution, hydrochloric acid solutions, hydrogen peroxide, mercuric chloride solution, methyl orange indicator solution, nitric acid, potassium dichromate or potassium permanganate, stannous chloride solution, sulfuric-phosphoric acid mixture, sulfuric-phosphoric acid-manganous sulfate mixture.	7. EQUIPMENT REQUIRED Laboratory balance, cold-finger condenser, crucibles, hot plate, muffle furnace, titration apparatus.
8. KEYWORD INDEX: Sulfur, sulfate, pyritic, coal, precipitation, titration, analysis.	
9. CROSS REFERENCE ID NUMBERS 02-01-03-02; 01-03-01-02, 01-03-02-01.	
10. REFERENCES A) PRIMARY SOURCE 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D 2492-68, "Standard Method of Test for Forms of Sulfur in Coal," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 387-388. B) BACKGROUND INFORMATION 057 ASTM Committee D-3 and D-5, "Gaseous Fuels; Coal and Coke," 1971 Annual Book of ASTM Standards, Part 19, D271, "Standard Method of Laboratory Sampling and Analysis of Coal and Coke," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 13-31. 312 Powell, Alfred R., "The Analysis of Sulfur Forms in Coal," Technical Paper No. 254, U.S. Bureau of Mines, 1921. 313 Krumin, Peter O., "The Interlaboratory Study of Methods for the Determination of Total Sulfur, Forms of Sulfur and Chlorine in Coal," Report of Investigation, OESRA, Ohio State University Engineering Experiment Station, 1960. (Continued on reverse side) C) FIELD APPLICATIONS	

TITLE GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF SULFATE SULFUR, PYRITIC
SULFUR AND ORGANIC SULFUR IN COAL (CONTINUED)

ID NO. 02-03-02-04

B) BACKGROUND INFORMATION

- 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, E200-67, "Standard Methods for Preparation, Standardization and Storage of Standard Solutions for Chemical Analysis," American Society for Testing and Materials, Philadelphia, PA., p. 868-885.
- 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1193, "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA., 1971, p. 196-197.

1. TITLE DETERMINATION OF SULFATE BY THE THORIN METHOD		2. IDENTIFICATION CODE 02-03-02-06
3. ABSTRACT OF METHODOLOGY Method involves titration of the sample with barium perchlorate solution using thorin as indicator. Thorin and barium react to form a deep red-colored complex when the endpoint is reached. The color varies in intensity with different solvents, and an organic solvent is the preferred medium for the analysis. The endpoint may be determined either spectrophotometrically or visually. When the spectrophotometric method is used, the preferred titration medium is 80 percent alcohol maintained at pH 5 with sodium acetate buffer. The endpoint may also be detected visually by viewing the solution through a didymium glass filter.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all samples (aqueous samples, acid gases absorbed in liquids) having sulfate content of less than 200 mg/liter.		
B) INTERFERENCES/LIMITATIONS Metal ions interfere, and can be removed by cation exchange. Phosphate interferes; with 100 mg/liter of sulfate, 10 and 20 mg/liter of phosphate give 2-3 percent positive error.		
C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of sulfur dioxide adsorbed in H ₂ O ₂ impinger solutions.		
5. OPERATIONAL PARAMETERS		
A) RANGE Sulfate content must not exceed 200 mg/liter.		
B) ACCURACY N/Q		
C) PRECISION Analysis of 2 test samples by 17 laboratories resulted in mean values of 394 and 21 mg/liter with standard deviations of 10 and 1.1 mg/liter, respectively.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Isopropanol, hydrogen peroxide, thorin indicator (1-(arsonophenylazo)-2-naphthol-3, 6-disulfonic acid), barium perchlorate, sulfuric acid standard.		Pipets, standard titration apparatus, standard laboratory glassware, cation exchange column (optional); spectrophotometer-titration assembly, didymium glass filter (optional).
8. KEYWORD INDEX: Sulfate, sulfur dioxide, aqueous effluents, titrimetry, spectrophotometry, thorin.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE		
314 "Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources," U. S. Environmental Protection Agency Federal Register 36, No. 247, P24890-1, December 23, 1971.		
185 "Methods for Chemical Analysis of Water and Wastes", Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 157-9.		
B) BACKGROUND INFORMATION		
315 California State Water Quality Control Board, "Water Quality Criteria," Pub. 3-A, 1963, p. 275.		
316 U.S. Public Health Service, "Drinking Water Standards," Public Health Service Pub. 956, 1962, p. 7.		
C) FIELD APPLICATIONS		
317 Atmospheric Emissions from Sulfuric Acid Manufacturing Processes, U.S. DHEW, PHS, Division of Air Pollution, Public Health Service Publication No. 999-AP-13, Cincinnati, Ohio, 1965.		
318 Corbett, P.F., "The Determination of SO ₂ and SO ₃ in Flue Gases," Journal of the Institute of Fuel, 24, 237-243, 1961.		
319 Matty, R.E., and E.K. Diehl, "Measuring Flue-Gas SO ₂ and SO ₃ ," Power, 101, 94-97, November 1957.		
320 Patton, W.F., and J.A. Brink, Jr., "New Equipment and Techniques for Sampling Chemical Process Gases," J. Air Pollution Control Association, 13, 162 (1963).		

1. TITLE DETERMINATION OF SULFATE IN SCRUBBER LIQUORS (SULFONAZO III TITRATION)		2. IDENTIFICATION CODE 02-03-02-06
3. ABSTRACT OF METHODOLOGY The total sulfur content of a scrubber liquor is determined by first passing the liquor through a cationic exchange resin. Next, H_2O_2 is added to the treated liquor to oxidize sulfides and sulfites to sulfate. The excess H_2O_2 is decomposed by boiling, and then acetone and the Sulfonazo III indicator are added to an aliquot of the treated liquor. The sulfate content is titrated with barium perchlorate with Sulfonazo III as the indicator. The endpoint is reached when the color changes from purple to blue.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE This procedure is applicable to the measurement of sulfate in aqueous wet scrubber process control liquors. The indicator, Sulfonazo III, is applicable to any sulfate titrations and is especially recommended for any procedure currently using thorin.		
B) INTERFERENCES/LIMITATIONS Cu^{+2} , Ni^{+2} , Co^{+2} , Zn^{+2} , Fe^{+2} and Pb^{+2} must be removed by ion exchange prior to titration. pH should be adjusted to <4. Treated solutions from the ion exchange column normally have a low enough pH.		
C) RECOMMENDED USE AREA Engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE 100 ppm sensitivity.		
B) ACCURACY Better than $\pm 5\%$.		
C) PRECISION Better than $\pm 5\%$.		
6. REAGENTS REQUIRED Dowex 50W-X8 (or equivalent) cation exchange column. Sulfonazo III, hydrogen peroxide, barium perchlorate.		7. EQUIPMENT REQUIRED Laboratory glassware, titration assembly.
8. KEYWORD INDEX: Analysis, sulfate titration, Sulfonazo III.		
9. CROSS REFERENCE ID NUMBERS 02-01-01, 02-01-02.		
10. REFERENCES		
A) PRIMARY SOURCE 321 Maddalone, R.F., A. Grant and C. Zee, "Final Report, Task 6; Development of Sulfonazo III Procedures for Sulfate," TRW Defense & Space Systems, Redondo Beach, California, February 1975 (EPA 68-02-1412).		
B) BACKGROUND INFORMATION 322 Budesinsky, B., and L. Krumlova, "Determination of Sulfur & Sulfate by Titration with Barium Perchlorate," <u>Anal. Chim. Acta.</u> , <u>39</u> , 375 (1967).		
C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF ALKALINITY BY ELECTROMETRIC TITRATION		2. IDENTIFICATION CODE 02-03-02-07
3. ABSTRACT OF METHODOLOGY		
The method involves the electrometric titration of the sample with a standard solution of strong acid. The endpoints of the titration are determined with a pH meter and are selected as the inflection points in the titration of sodium carbonate with sulfuric acid, (e.g., a bicarbonate endpoint at pH 4.5, and a carbonate endpoint at pH 8.3).		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous streams (liquid and slurry discharges) including drinking, surface and saline water, and industrial wastes. Samples having high concentrations of mineral acids should be titrated to pH 3.9 (see Ref. 024). B) INTERFERENCES/LIMITATIONS Interferences include large quantities of salts of weak organic and inorganic acids (e.g., silicic acid) and oil and grease which may coat the pH electrode. C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of total alkalinity of all aqueous samples, including saline samples.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method measures all concentration ranges of alkalinity, using samples having volumes of 50 ml. B) ACCURACY The accuracy (bias) of 40 analysts in 17 laboratories analyzing synthetic water samples having 8, 9, 113 and 119 mg/liter alkalinity as CaCO_3 was reported as +0.85, +2.0, -9.3, -8.8 mg/liter CaCO_3, respectively. C) PRECISION In a single laboratory (MDJABL) using surface water samples at an average concentration of 122 mg CaCO_3/liter, a standard deviation of ± 3 was obtained.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
0.02N standard hydrochloric acid; indicators (bromocresol green, methyl orange, methyl purple, methyl red, phenolphthalein).		Pipets, electrometric titration apparatus, Erlenmeyer flasks.
8. KEYWORD INDEX: Alkalinity, aqueous effluents (liquid/slurry), electrometric titration.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01; 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 3-4. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D-1067, "Standard Methods for Test for Acidity or Alkalinity of Water," American Society for Testing and Materials, Philadelphia, PA., 1971, Method B., p. 138. C) FIELD APPLICATIONS 323 Barnes, Ivan, "Field Measurement of Alkalinity and pH," U.S. Geol. Survey Water-Supply Paper 1535-H, 17 p. (1964). 324 Eaton, F.M., "Formulas for Estimating the Drainage and Gypsum Requirements of Irrigation Waters," Texas Agr. Expt. Sta. Misc. Pub. 111, 1954. 325 U.S. Salinity Laboratory Staff, "Diagnosis and Improvement of Saline and Alkali Soils," U.S. Dept. Agriculture, Agric. Handbook, 60, p. 81 (1954).		

1. TITLE DETERMINATION OF BROMIDE BY TITRIMETRY		2. IDENTIFICATION CODE 02-03-02-08
3. ABSTRACT OF METHODOLOGY After pretreatment with calcium oxide for removal of interferences (iron, manganese and organic matter), the sample is divided into 2 aliquots. The first sample is treated with bromine water for conversion of iodide to iodate, then is titrated with phenyl arsine oxide (PAO) or sodium thiosulfate using starch as the indicator for the determination of iodide. The endpoint is determined by means of a pH meter rather than a pH indicator. The second aliquot is analyzed for iodide plus bromide by conversion of these species to iodate and bromate with calcium hypochlorite. Excess hypochlorite is decomposed with sodium formate. The sample is then titrated with PAO or thiosulfate, as above. Bromide is then calculated by difference.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid and slurry) streams, including drinking, surface and saline waters, domestic and industrial wastes.		
B) INTERFERENCES/LIMITATIONS Interferences caused by iron, manganese and organic matter are removed by calcium oxide pretreatment. Color interferences are eliminated by use of pH meter.		
C) RECOMMENDED USE AREA This is the recommended compliance procedure for bromide determinations of all aqueous industrial effluents.		
5. OPERATIONAL PARAMETERS		
A) RANGE Concentration range is 2 to 20 mg/liter of bromide.		
B) ACCURACY 96, 83, 97, 99% recoveries on mixed domestic and industrial waste effluent having concentrations of 2.8, 5.3, 10.3 and 20.3 mg/liter of bromide.		
C) PRECISION Standard deviations of ± 0.13 , ± 0.37 , ± 0.38 , ± 0.44 and ± 0.42 mg/liter on samples above having concentrations of 0.3, 2.8, 5.3, 10.3 and 20.3 mg/liter, respectively.		
6. REAGENTS REQUIRED Acetic acid, bromine water, calcium carbonate, calcium hypochlorite, calcium oxide, hydrochloric acid, potassium iodide, phenylarsine oxide, sodium thiosulfate, starch solution, amylose indicator.		7. EQUIPMENT REQUIRED Standard laboratory glassware, titration apparatus, pH meter.
8. KEYWORD INDEX: Bromide, aqueous effluents, titrimetric method.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01; 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 14-18.		
B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, Method D1246-C, "Standard Methods of Test for Iodide and Bromide in Industrial Water and Industrial Wastewater," American Society for Testing and Materials, Philadelphia, PA., 1973, p. 331-6.		
C) FIELD APPLICATIONS 326 Shiota, K., I. Iwasaki and S. Tusumi, "Determination of Bromide by Its Catalytic Action," <u>Nippon Kagakii Tasshi</u> , 80 , 753-7 (1959), <u>Chem. Abstr.</u> , 54 , No. 19278d.		

1. TITLE DETERMINATION OF CHLORIDE BY TITRIMETRY	2. IDENTIFICATION CODE 02-03-02-09
3. ABSTRACT OF METHODOLOGY Method involves acidification of sample, followed by titration with dilute mercuric nitrate solution, in the presence of a small amount of mixed diphenylcarbazone-bromophenol blue indicator. The optimum pH range for the titration is pH 3.0-3.6. The proper pH for the titration is easily obtained by adding bromphenol blue indicator and slowly adding dilute nitric acid or sodium hydroxide to adjust the pH of the sample. The formation of the stable blue-violet mercury diphenylcarbazone complex indicates the endpoint of the titration, which can be determined visually by observing the persistent blue-violet color, or spectrophotometrically, at 530 nm.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid and slurry) streams, including drinking, surface and saline waters, domestic and industrial effluents.	
B) INTERFERENCES/LIMITATIONS Anions and cations at concentrations normally found in surface waters do not interfere (approximately 1 to 100 ppm range). Sulfites interfere, but are removed by treatment with hydrogen peroxide.	
C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of chloride in all aqueous effluents with moderate anion and cation levels (see above).	
5. OPERATIONAL PARAMETERS	
A) RANGE Method is suitable for all ranges of chloride; sample aliquots of 10 to 20 mg Cl per 50 ml should be used.	
B) ACCURACY Accuracy results (bias) of 42 analysts in 18 laboratories on samples having chloride increments as 17, 18, 91, 97, 382, 398 mg/liter were +0.4, +0.6, +0.1, -0.5, -2.3, and -4.7 respectively, in mg/liter.	
C) PRECISION In a single (MDQARL) laboratory, using surface water samples at an average concentration of 34 mg/liter Cl, the standard deviation was ± 1.0 .	
6. REAGENTS REQUIRED Mercuric nitrate solution; diphenylcarbazone-bromophenol blue indicator.	7. EQUIPMENT REQUIRED Standard laboratory equipment; titration assembly.
8. KEYWORD INDEX: Chloride, aqueous effluents, titrimetric method.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01; 01-02-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 29-30.	
B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water: Atmospheric Analysis," Part 23, D512-67, "Standard Methods of Test for Chloride Ion in Industrial Water and Industrial Wastewater," Referee Method A, American Society for Testing and Materials, Philadelphia, PA., 1973, p. 273. 327 Dubsky, J.V., and J. Trtilik, "Microvolumetric Analysis Using Diphenylcarbazide and Diphenylcarbazone as Indicators (Mercurimetry)," <i>Mikrochemie</i> , V. 12, 315 (1933).	
C) FIELD APPLICATIONS 328 Clarke, F.E., "Determination of Chloride in Water," <i>Anal. Chem.</i> , 22, 553, 1458 (1950). 327 Eaton, F.M., "Formulas for Estimating the Drainage and Gypsum Requirements of Irrigation Waters," Texas Agr. Expt. Sta. Misc. Rept., 111, 1954. 330 Taylor, E.W., "The Examination of Waters and Water Supplies," 7th ed., Boston, Little, Brown & Co., 1958, 841 p. 331 U.S. Public Health Service, "Drinking Water Standards," Public Health Service Pub. 956, p. 7 (1956).	

1. TITLE DETERMINATION OF TOTAL CYANIDE BY VOLUMETRIC TITRATION OR SPECTROPHOTOMETRY	2. IDENTIFICATION CODE 02-03-02-10
3. ABSTRACT OF METHODOLOGY The sample to be analyzed, which contains complexed cyanide, is subjected to reflux-distillation; the cyanide is released and absorbed as HCN in a sodium hydroxide scrubber. The cyanide ion in the absorbing solution is then determined by volumetric titration or by colorimetry. The titrimetric measurement uses silver nitrate as the titrant and p-dimethylaminobenzalrhodanine indicator. The first change in color from yellow to brownish-pink signals the endpoint of the titration. In the colorimetric measurement, the cyanide is converted to cyanogen chloride by reaction with chloramine-T at pH less than 8. A solution of pyridine-pyrazolone or pyridine-barbituric acid is then added, and absorbance is measured at 620 nm or 578 nm, respectively.	
4. APPLICATION: Compliance, environmental assessment. A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including drinking, surface, and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Oxidizing agents (chlorine) interfere, but can be removed by adding ascorbic acid until KI-starch test paper remains colorless. Sulfides interfere, but may be removed by treatment with cadmium carbonate. Fatty acids also interfere, but may be removed by acidification and solvent extraction. C) RECOMMENDED USE AREA This is the recommended compliance method for the determination of total cyanide in aqueous effluents, especially complexed cyanide, which cannot be determined by S.I.E. method (see 02-03-02-01).	
5. OPERATIONAL PARAMETERS A) RANGE Volumetric titration measures cyanide concentrations greater than 1 mg/liter in 0.2 mg/200 ml of absorbing liquid. Colorimetric procedure measures concentrations below 1 mg/liter of cyanide and is sensitive to 0.02 mg/liter. B) ACCURACY Recoveries of 85% and 102% were obtained in a single laboratory (MDQARL) using mixed industrial and domestic waste samples having cyanide concentrations of 0.28 and 0.62 mg/liter cyanide. C) PRECISION Standard deviations of ± 0.005, ± 0.007, ± 0.031 and ± 0.094 were obtained in a single laboratory (MDQARL) using mixed industrial and domestic waste samples with concentrations of 0.06, 0.13, 0.28, and 0.62 mg/liter cyanide.	
6. REAGENTS REQUIRED Sodium hydroxide, cadmium carbonate, ascorbic acid, cuprous chloride, sulfuric acid, sodium dihydrogen phosphate, standard cyanide solution, silver nitrate solution, rhodanine indicator, Chloramine T, color reagents (pyridine-barbituric acid; pyridine-pyrazolone solution)	7. EQUIPMENT REQUIRED Reflux distillation apparatus microburet; spectrophotometer.
8. KEYWORD INDEX: Cyanide, aqueous effluents, volumetric titration, spectrophotometry.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02; 02-03-02-01.	
10. REFERENCES A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 40-46. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, D2036-72, "Standard Methods of Test for Cyanides in Water," Referee Method A, American Society for Testing and Materials, Philadelphia, PA., 1973, p. 498. 332 Bark, L.S., and H.G. Higson, "Investigation of Reagents for the Colorimetric Determination of Small Amounts of Cyanide," <i>Talanta</i>, 2, 471-9 (1964). C) FIELD APPLICATIONS 333 Etlly, C.T., "Recovery of Cyanides by Modified Serfass Distillation," <i>JNPCE</i>, 40, 848-56 (1968). 331 U.S. Public Health Service, "Drinking Water Standards," Public Health Service Pub. 956, p. 6 (1952).	

1. TITLE DETERMINATION OF IODIDE BY TITRIMETRY		2. IDENTIFICATION CODE 02-03-02-11
3. ABSTRACT OF METHODOLOGY		
The sample is first pretreated with calcium oxide in order to reduce interferences caused by iron, manganese and organic matter. The sodium acetate-buffered sample is then oxidized with bromine to iodate, and the excess bromine is removed with sodium formate. Iodine, which is equivalent to the iodide present in the sample, is then liberated by the addition of potassium iodide to an acidic solution. The iodine is then titrated using standard thiosulfate solution, using starch as the indicator. The endpoint may be determined with a pH meter, or by visual observation of the light yellow color.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous (liquid and slurry) streams, including drinking, surface and saline waters, sewage and industrial waste effluents. B) INTERFERENCES/LIMITATIONS Iron, manganese and organic material interfere, but these can be removed by pretreatment with calcium oxide. C) RECOMMENDED USE AREA This is the recommended compliance method for determination of iodide in all aqueous effluents.		
5. OPERATIONAL PARAMETERS		
A) RANGE 2 to 20 mg/liter iodide. B) ACCURACY Recoveries of 80, 97, 97 and 92% were obtained in a single laboratory (MDQARL) using mixed domestic and industrial waste effluent, at concentrations of 1.6, 4.1, 6.6, 11.6 and 21.6 mg/liter iodide. C) PRECISION Standard deviations of ± 0.23, ± 0.17, ± 0.10, ± 0.06 and ± 0.50 mg/liter were obtained for the samples described in 5 (b) above.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Acetic acid, bromine water, calcium oxide, potassium iodide, sodium acetate, sodium formate, sulfuric acid, phenylarsine oxide, amylose indicator, sodium thiosulfate.		Standard laboratory glassware; titration assembly, pH meter (optional).
8. KEYWORD INDEX: Iodide, aqueous effluents, titrimetry.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 74-7. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, D1246C, "Standard Methods of Test for Iodide and Bromide in Industrial Water and Industrial Wastewater," American Society for Testing and Materials, Philadelphia, PA., 1973, p. 331-3. 333 Kolthoff, I.M., and E.B. Sandell, "Textbook of Quantitative Inorganic Analysis," New York, Macmillan Co., 3rd ed., 1952, p. 585. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF NITRATE NITROGEN BY BRUCINE METHOD	2. IDENTIFICATION CODE 02-03-02-12
3. ABSTRACT OF METHODOLOGY	
Method is based on a spectrophotometric determination of the yellow-colored reaction product of the alkaloid brucine with nitrate in an acid medium. The sample is prepared by adjustment of the pH to 7.0 with acetic acid or sodium hydroxide, and filtration to remove turbidity. After treatment to remove interference (see 4(b) below), the sample is acidified with concentrated sulfuric acid. Brucine-sulfanilic acid reagent is then added, and the sample is heated in a boiling water bath. After cooling, the colored complex is determined spectrophotometrically at 410 nm.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to most aqueous streams including drinking, surface and saline water, domestic and industrial effluents. This method is especially useful on samples of high salinity. B) INTERFERENCES/LIMITATIONS Dissolved organic matter interferes, but can be removed by addition of suitable reagents. Addition of NaCl to blanks, standard and samples compensates for interfering chloride. Sodium arsenite eliminates interference due to residual chlorine (up to 5 mg/liter). Interference up to 1 mg/liter nitrite is eliminated by use of sulfanilic acid. Other strong redox agents interfere. Iron and manganese interfere at concentrations greater than 1 mg/liter. C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of all nitrate nitrogen in aqueous effluents not exceeding limitations cited above.	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.1 to 2 mg nitrate nitrogen/liter. B) ACCURACY Accuracy results (as bias in mg N/liter) obtained by 27 analysts in 15 laboratories on samples containing 0.16, 0.19, 1.08 and 1.24 mg N/liter were -0.01, +0.2, +0.04 and +0.04 mg N/liter respectively. C) PRECISION Precision (as standard deviations in mg N/liter) obtained by 27 analysts in 15 laboratories on samples containing 0.16, 0.19, 1.08 and 1.24 mg N/liter were 0.092, 0.083, 0.245, and 0.214 mg N/liter, respectively.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Sodium chloride, sulfuric acid, brucine-sulfanilic acid, potassium nitrate, acetic acid, sodium hydroxide.	Spectrophotometer or filter photometer for optical density measurement at 410 nm; glass sample tubes; neoprene-coated wire racks to hold sample tubes; water bath (100°C), water bath (10 to 150°C).
8. KEYWORD INDEX: Nitrate nitrogen, brucine, liquid/slurry, spectrophotometry, filter photometry.	
9. CROSS REFERENCE ID NUMBERS 01-02, 01-02-02-01.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 197-200. B) BACKGROUND INFORMATION ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, D992-71, "Standard Method of Test for Nitrate Ion in Water," American Society for Testing and Materials, Philadelphia, PA., 1973, p. 363. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, Method 213-C, p. 461. C) FIELD APPLICATIONS 334 Jenkins, D., and L. Medsken, "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine and Fresh Waters," <u>Anal. Chem.</u>, 36, 610 (1964). 335 Fishman, M.J., G.F. Scarbro and H. Skougstad, "Diazotization Method for Nitrate and Nitrite," <u>Amer. Water Works Assoc. J.</u>, 56, 633 (1964). 336 Rider, B.F., and M.G. Mellon, "Colorimetric Determination of Nitrites," <u>Ind. Eng. Chem., Anal. Ed.</u>, 18, 76 (1945).	

2. IDENTIFICATION CODE	
1. TITLE DETERMINATION OF NITRATE-NITRITE NITROGEN BY CADMIUM REDUCTION METHOD	02-03-02-13
3. ABSTRACT OF METHODOLOGY	
Method involves reduction of nitrate to nitrite by passage of a filtered sample through a column containing granulated copper-cadmium. (The sample may be prefiltered through a glass filter or a 0.45 μ membrane filter to eliminate interference due to turbidity.) A typical reduction column is shown in Figure 02-03-02-13A. The column may be constructed from 2 pieces of tubing joined end to end, or from a 100-ml pipet. The cadmium granules (new or used) are cleaned with dilute HCl and copperized with a 2% solution of copper sulfate. The column effluent is then used to diazotize sulfanilamide, which is then treated with N(1-naphthyl) ethylenediamine dihydrochloride to form an azo dye. The dye is then determined spectrophotometrically at 540 nm. A simple nitrite nitrogen value can be obtained by omitting the copper-cadmium reduction step. (See 02-03-02-14.) A simple nitrate nitrogen value can be obtained from the difference between the nitrate-nitrite and simple nitrite determinations.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to most aqueous streams including drinking, surface and saline water, domestic and industrial effluents. B) INTERFERENCES/LIMITATIONS Suspended particle can be removed by filtration; turbidity can be removed by treatment with zinc sulfate. Addition of EDTA eliminates interferences due to high concentrations of trace metals (iron, copper, etc.). Oil and grease can interfere by coating the surface of the cadmium; this is eliminated by extraction with an organic solvent. C) RECOMMENDED USE AREA This is the recommended compliance method for determination of total nitrate-nitrite nitrogen and/or nitrite and nitrate nitrogen alone, in aqueous effluents (liquids and slurries).	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.01 to 10 mg/liter nitrate-nitrite nitrogen; range may be extended with sample dilution. B) ACCURACY Recoveries of 100%, 102% and 100% were obtained in a single laboratory (MDQARL) using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg nitrate-nitrite nitrogen/liter. C) PRECISION The standard deviations of ± 0.005, ± 0.004, ± 0.005 and ± 0.01 were determined on samples cited above.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Granulated cadmium; copper-cadmium; ammonium chloride-EDTA, sulfanilamide and N(1-naphthyl)-ethylenediamine dihydrochloride, zinc sulfate, sodium hydroxide, ammonium hydroxide, copper sulfate, stock nitrite and nitrate solutions.	Reduction column (see Figure 02-03-02-13A); spectrophotometer for use at 540 nm, with path length of 1 cm or longer.
8. KEYWORD INDEX: Nitrate-nitrite nitrogen, aqueous effluents, cadmium reduction method, spectrophotometry.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-02, 01-02-02-01; 02-03-02-14.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 201-206. B) BACKGROUND INFORMATION 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, Method 213-C, p. 458. C) FIELD APPLICATIONS 337 Henrikson, A., and Selmer-Olsen, "Automatic Methods for Determining Nitrate and Nitrite in Water and Soil Extracts," <i>Analyst</i>, 95, 514-518, May 1970. 338 Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water With Analog and Digital Data Record," <i>Advances in Automated Analysis</i>, Technicon International Congress, Vol. 11, 132-45, 1969. 339 Brewer, P., and J.P. Riley, "The Automatic Determination of Nitrate in Sea Water," <i>Deep Sea Research</i>, 12, 765-72, 1965.	

TITLE DETERMINATION OF NITRATE-NITRITE NITROGEN BY CADMIUM REDUCTION
METHOD (CONTINUED)

ID NO. 02-03-02-13

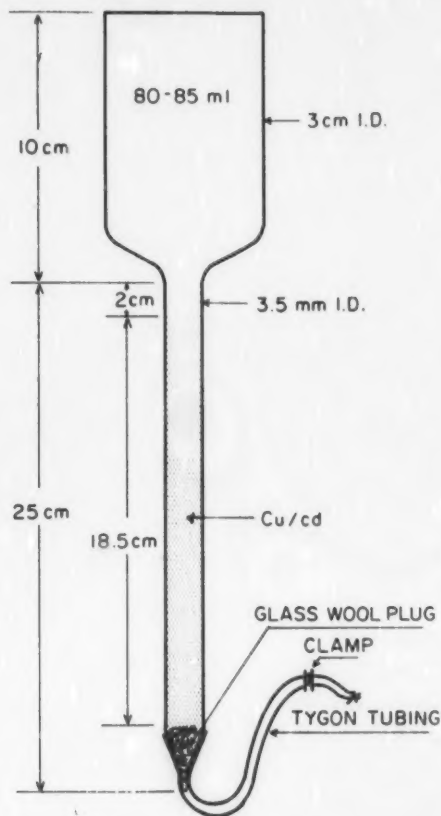


Figure 02-03-02-13A. Reduction Column (Reference 185).

1. TITLE DETERMINATION OF NITRITE NITROGEN BY SPECTROPHOTOMETRY	2. IDENTIFICATION CODE 02-03-02-14
3. ABSTRACT OF METHODOLOGY The pH of the sample is first adjusted to pH 6 with 1:3 hydrochloric acid. The sample is then treated with sulfanilamide and N-(1-naphthyl) ethylenediamine dihydrochloride. The nitrite diazotizes the sulfanilamide, and subsequent coupling of the species to the diamine salt results in the formation of a red-colored azo dye. The dye is then determined spectrophotometrically at 540 nm.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to most aqueous streams (liquids and slurries) including drinking, surface and saline waters, domestic and industrial wastes.	
B) INTERFERENCES/LIMITATIONS Strong oxidants or reductants interfere; high alkalinity (>600 mg/liter) gives low results due to shift in pH.	
C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of nitrite nitrogen.	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.01 to 1.0 mg nitrite nitrogen per liter.	
B) ACCURACY N/Q	
C) PRECISION N/Q	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
Distilled water; buffer-color reagent, (hydrochloric acid sulfanilamide, N-(1-naphthyl) ethylenediamine dihydrochloride, sodium acetate); nitrite solutions.	Spectrophotometer for use at 540 nm with 1 cm or greater cells; 50 ml Nessler tubes or 50 ml volumetric flasks.
8. KEYWORD INDEX: Nitrite nitrogen, aqueous effluents, spectrophotometry.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02; 02-03-02-13.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 215-16.	
B) BACKGROUND INFORMATION 204 "Standard Methods for the Examination of Water and Wastewater," 13th ed., Washington, D. C., 1971, p. 458.	
C) FIELD APPLICATIONS 340 Henrikson, A., and Selmer-Olsen, "Automatic Methods for Determining Nitrate and Nitrite in Water and Soil Extracts," <u>Analyst</u> , 95, 514-18 (1970).	

1. TITLE DETERMINATION OF PHOSPHOROUS (ALL FORMS) BY SINGLE REAGENT METHOD	2. IDENTIFICATION CODE 02-03-02-15
3. ABSTRACT OF METHODOLOGY	
Figure 02-03-02-15A (from Reference A) shows the analytical scheme for differentiation of the various phosphorous (P) forms, which is based on specific sample pretreatments. Total P is determined using the total phosphorous method with no prior filtration. Total orthophosphate is measured by colorimetric detection of a blue-colored complex formed by reaction of a sample with ammonium molybdate and antimony potassium tartrate. Total hydrolyzable P is determined by sulfuric acid hydrolysis procedure and colorimetry, minus predetermined orthophosphates. Finally, total organic P is measured by persulfate digestion and colorimetry, and minus hydrolyzable P and orthophosphate. Dissolved P includes all P present in the filtrate of the sample which has passed a membrane filter. Dissolved orthophosphate is determined by colorimetry, as above. Dissolved hydrolyzable P is measured by sulfuric acid hydrolysis and colorimetry, minus predetermined dissolved orthophosphates. Dissolved organic P is measured by persulfate digestion and colorimetry, minus dissolved hydrolyzable P and orthophosphate. The colorimetric finish consists of adjusting the pH to 7 ± 0.2 and adding 8 ml of a combination reagent. The combination reagent consists of: 50 ml 5N H_2SO_4, 5 ml antimony potassium tartrate solution (1.3715 g/500 ml), 15 ml ammonium molybdate solution (20 g/500 ml), and ascorbic acid solution (0.1 M). The resultant color is measured at 650 or 680 nm with a spectrophotometer.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including drinking, surface and saline waters, domestic and industrial effluents; it may also be applicable to sediment-type samples, sludges, etc. B) INTERFERENCES/LIMITATIONS High iron concentrations can cause precipitation of phosphorous. Copper, iron and silicate may interfere at very high concentrations (much greater than sea level concentrations). Arsenate, at concentrations greater than sea water, may interfere. Mercury chloride (used as sample preservative) interferes when the chloride level of the sample is low; this is overcome by addition of a minimum of 50 mg/liter of sodium chloride. C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of phosphores (all forms) in aqueous effluents.	
5. OPERATIONAL PARAMETERS	
A) RANGE 0.01 to 0.5 mg phosphorous/liter. B) ACCURACY The accuracy (bias) obtained by 33 analysts in 19 laboratories using samples containing 0.110, 0.132, 0.772 and 0.882 mg P/liter were +0.003, +0.016, +0.023, -0.008 mg P/liter. C) PRECISION The precisions obtained on the above samples were 0.033, 0.051, 0.130 and 0.128 mg P/liter, respectively.	
6. REAGENTS REQUIRED Sulfuric acid, antimony potassium tartrate, ammonium molybdate, ascorbic acid, ammonium persulfate, standard phosphorous solution, sodium hydroxide, phenolphthalein.	7. EQUIPMENT REQUIRED Spectrophotometer or filter photometer; acid-washed glassware; 0.45µ membrane filter; standard laboratory equipment.
8. KEYWORD INDEX: Phosphorous, aqueous effluents, spectrophotometry, ammonium molybdate, antimony potassium tartrate.	
9. CROSS REFERENCE ID NUMBERS 01-02-02-01; 01-02-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 249-55. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-23, "Water; Atmospheric Analysis," Part 23, D. 515-72, "Standard Methods of Test for Phosphate in Industrial Water," American Society for Testing and Materials, Philadelphia, PA., 1973, p. 388. 341 Gales, H., Jr., E. Julian and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water," J. Am. Water Works Assoc., 58, No. 10, 1363 (1966). C) FIELD APPLICATIONS 342 Murphy, J., and J. Riley, "A Modified Single Solution for the Determination of Phosphate in Natural Waters," Anal. Chem. Acta., 27, 31 (1962).	

TITLE DETERMINATION OF PHOSPHOROUS (ALL FORMS) BY SINGLE REAGENT METHOD (CONTINUED)

ID NO. 02-03-02-15

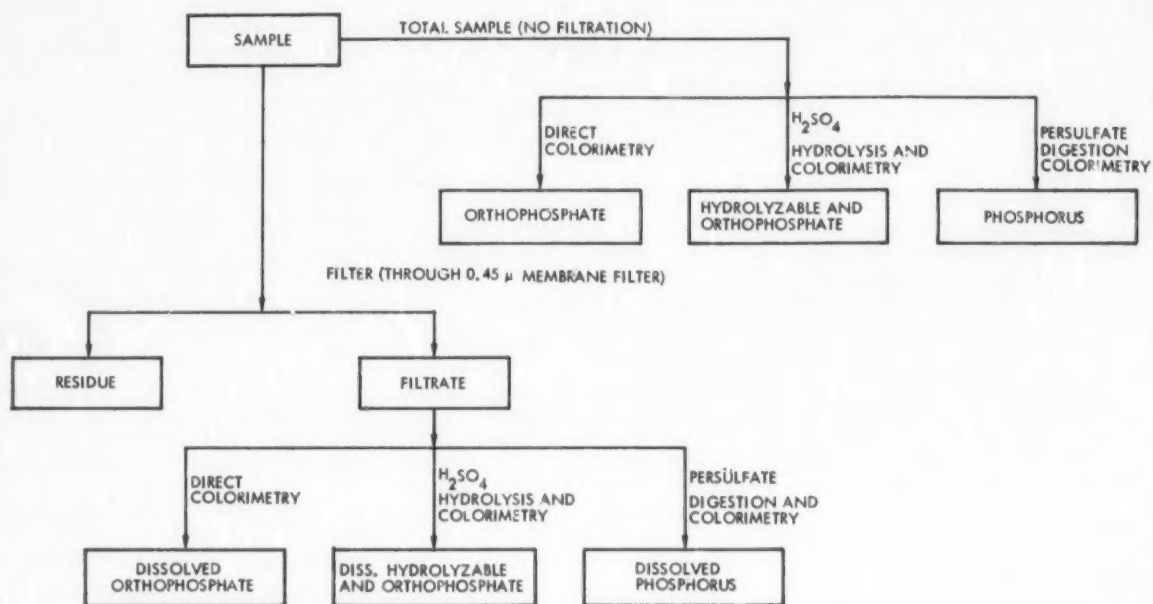


Figure 02-03-02-15A. Analytical Scheme for Differentiation of Phosphorus Forms (Ref. 185).

1. TITLE TURBIDIMETRIC DETERMINATION OF SULFATE		2. IDENTIFICATION CODE 02-03-02-16
3. ABSTRACT OF METHODOLOGY		
Method involves precipitation of sulfate as barium sulfate using barium chloride and a suspending agent (gelatin in some cases). The resultant turbidity is determined using a colorimeter, nephelometer, or transmission spectrophotometer and is compared to a curve obtained using standard sulfate solutions.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including drinking and surface waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Excessive color and suspended matter interfere; this is overcome by blank determinations using samples not treated with barium chloride. Silica in excess of 500 mg/liter will interfere. C) RECOMMENDED USE AREA This is the recommended level 1 environmental assessment procedure for determination of sulfate in aqueous samples.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method can be used for all concentration ranges of sulfate; aliquots of 40 mg sulfate/liter are recommended. B) ACCURACY Accuracy results (bias) obtained by 34 analysts in 16 laboratories on samples containing 8.6, 9.2, 110, 122, 188 and 199 mg/liter sulfate were -0.3, -0.8, -3.3, -4.1, +0.1, and -3.4 mg/liter, respectively. C) PRECISION Precisions (as standard deviation) obtained on samples described above were 2.30, 1.78, 7.86, 7.50, 9.58 and 11.8 mg/liter, respectively.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Barium chloride; proprietary reagents, such as Hach Sulfaver, may be used.		Colorimeter, spectrophotometer or nephelometer.
8. KEYWORD INDEX: Sulfate, aqueous effluents, turbidimetry.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 277. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, D516-68, "Standard Methods of Test for Sulfate Ion in Industrial Water and Industrial Wastewater," American Society for Testing and Materials, Philadelphia, PA., 1973, Method B, p. 425. 024 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, Method 213-C, p. 461. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL AND DISSOLVED SULFIDE USING TITRIMETRIC IODINE METHOD		2. IDENTIFICATION CODE 02-03-02-17
3. ABSTRACT OF METHODOLOGY		
Method involves stripping of sulfides from an acidified sample by means of inert gas, followed by collection of the sulfide in a zinc acetate solution with formation of zinc sulfide suspension. The suspension is treated with excess iodine; the iodine reacts with the sulfide under acidic conditions. Unreacted iodine is titrated with thiosulfate solution, and the quantity of iodine consumed by sulfide is determined by difference using starch as the indicator.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including drinking, surface and saline waters, domestic and industrial effluents.		
B) INTERFERENCES/LIMITATIONS Sulfite, thiosulfate, hydrosulfite, and other reduced sulfur compounds which are unstable in acid, interfere. Volatile iodine-consuming substances give high results. Acid insoluble sulfides (e.g., CuS) are not determined by this method.		
C) RECOMMENDED USE AREA This is the recommended compliance procedure for determination of total and dissolved sulfides.		
5. OPERATIONAL PARAMETERS		
A) RANGE Sulfide concentrations above 1 mg/liter can be measured.		
B) ACCURACY Accuracy of the method has not been determined.		
C) PRECISION Precision of the method has not been determined.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Zinc acetate solution, iodine, sodium thiosulfate solution, inert gas, starch indicator.		Standard laboratory equipment, standard titration apparatus.
8. KEYWORD INDEX: Sulfide (total and dissolved), aqueous effluents, titrimetric iodine method.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 284.		
B) BACKGROUND INFORMATION 204 Taras, H.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, Method 228A, p. 551-5.		
C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF SULFITE USING TITRIMETRIC IODIDE-IODATE METHOD		2. IDENTIFICATION CODE 02-03-02-18
3. ABSTRACT OF METHODOLOGY		
Method involves titration of an acidified sample containing starch indicator with standard potassium iodide-iodate titrant to a faint permanent blue end point, which is determined visually. The temperature of the sample should be maintained below 50°C. The sample should be analyzed as quickly as possible, and care should be taken to allow as little contact with air as possible (e.g., the sample should not be filtered; the buret tip should be kept below the surface of the sample; closed containers should be used, etc.) to avoid oxidation of sulfite to sulfate.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including drinking and surface waters, sewage and industrial wastes. B) INTERFERENCES/LIMITATIONS Organic compounds, ferrous iron and sulfide, and other oxidizable substances are positive interferences. Nitrite gives negative interference; this can be eliminated by addition of sulfamic acid. Copper and other heavy metals interfere; these are removed with EDTA. C) RECOMMENDED USE AREA This is the recommended compliance procedure for the determination of sulfite for aqueous samples such as ash dewatering effluents, and dehydration waters.		
5. OPERATIONAL PARAMETERS		
A) RANGE 2 to 3 mg/liter sulfite. B) ACCURACY Accuracy of the method has not been determined. C) PRECISION Precision of the method has not been determined.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Standard potassium iodide-iodate solutions, starch solution, EDTA (optional), sulfamic acid (optional).		Standard titration assembly; standard laboratory equipment.
8. KEYWORD INDEX: Sulfite, aqueous effluent, titrimetry, iodine-iodate.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," National Environmental Research Center, EPA No. 625/6-74-003, Washington, 1974, p. 285. B) BACKGROUND INFORMATION 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," Part 23, Method D1339C, "Standard Methods of Test for Sulfite Ion in Industrial Water," American Society for Testing and Materials, Philadelphia, PA., 1973, p. 436. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D. C., 1971, Method 158, p. 337-8. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF CHLORIDE BY COLORIMETRY		2. IDENTIFICATION CODE 02-03-02-19
3. ABSTRACT OF METHODOLOGY		
Method involves treatment of the sample with ferric ammonium sulfate (57% w/v) and mercuric thiocyanate (0.3% w/v). The chloride ion reacts with the mercuric thiocyanate producing thiocyanate ion, which in turn combines with ferric ion to form red-colored ferric thiocyanate. The intensity of the color is then measured spectrophotometrically at a wavelength of 463 nm. The concentration of chloride is then determined by comparison of the absorbance of the sample to a calibration curve prepared from reference standards containing chloride ion.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE Method is applicable to aqueous (liquid and slurry) streams, including surface waters, domestic and industrial effluents. B) INTERFERENCES/LIMITATIONS Excessive color interferes. Bromides, iodides, cyanides, thiosulfates and nitrites interfere. C) RECOMMENDED USE AREA This is an alternative recommended engineering evaluation R&D procedure for determination of chloride in aqueous effluents (see 02-03-02-09).		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is applicable to all ranges of chloride, if suitable aliquots are used. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Ferric ammonium sulfate; mercuric thiocyanate solution in methanol, sodium chloride.	Nessler tubes; filter photometer; spectrophotometer.	
8. KEYWORD INDEX: Chloride, aqueous effluents, ferric thiocyanate, colorimetry, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-02-01, 01-02-02-02; 02-03-02-09.		
10. REFERENCES		
A) PRIMARY SOURCE 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract #68-02-1393, July 1975. B) BACKGROUND INFORMATION 343 Horowitz, W. (ed.), "Official Methods for Analysis of the Association of Official Analytical Chemists," 11th ed., 1970. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF NITRATE NITROGEN BY PHENOL DISULFONIC ACID METHOD		2. IDENTIFICATION CODE 02-03-02-20
3. ABSTRACT OF METHODOLOGY		
The sample is pretreated for the removal of interferences with: (1) aluminum hydroxide suspension to decolorize the sample, and (2) silver sulfate solution for the removal of chloride. Nitrite is then converted to nitrate with sulfuric acid, followed by potassium permanganate or hydrogen peroxide. The pretreated sample is then neutralized to pH 7, then is treated with phenol disulfonic acid reagent to form the characteristic yellow product. A standard hydroxide solution is then added until maximum yellow color is achieved. Flocculent hydroxides are then removed by passage through a filter, or addition of EDTA, until all turbidity redissolves. The yellow color is then determined spectrophotometrically at 410 nm.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is primarily used to measure the nitrate content of impingers used to sample flue gas for NO₂. B) INTERFERENCES/LIMITATIONS Chloride interferes, but can be eliminated using silver sulfate. Nitrite interferes, but can be oxidized to nitrate with permanganate or hydrogen peroxide. Excessive color interferes, but can be decreased using an aluminum hydroxide suspension. C) RECOMMENDED USE AREA This method is used in compliance testing of stacks for NO₂ content (see 01-01-01-02).		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is sensitive to 1 µg nitrate (10 ppm in 100-ml sample). B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Silver sulfate, phenol disulfonic acid, standard and stock nitrate solutions; aluminum hydroxide suspension, sulfuric acid, potassium permanganate, sodium hydroxide, hydrogen peroxide, EDTA.	Spectrophotometer for use at 410 nm.	
8. KEYWORD INDEX: Nitrate nitrogen, nitrogen dioxide, impingers, liquid/slurry, phenol disulfonic acid, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-01-01-02; 01-02-02-01, 01-02-02-02; 02-03-02-12.		
10. REFERENCES		
A) PRIMARY SOURCE 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of Standards, Part 23, D1608, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 387. B) BACKGROUND INFORMATION 343 Horowitz, W. (ed.), "Official Methods for Analysis of the Association of Official Analytical Chemists," 11th ed., 1970. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL SOLIDS		2. IDENTIFICATION CODE 02-03-02-21
3. ABSTRACT OF METHODOLOGY		
Total solids is defined as the sum of homogeneous suspended and dissolved materials in a sample. An aliquot of the sample to be determined is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness (and constant weight) at 103-105°C on a steam bath.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, as well as domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Large floating particles or submerged agglomerates should be removed from the test sample. Floating grease and oil should be dispersed with a blender before aliquoting. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE 10-20,000 mg/liter solids. B) ACCURACY N/Q C) PRECISION A standard deviation of 0.9 was found on samples of settled effluents.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
N/A	Evaporating dishes (porcelain preferred; vycor or platinum), desiccator, analytical balance.	
8. KEYWORD INDEX: Total solids, aqueous effluents, gravimetric method.		
9. CROSS REFERENCE ID NUMBERS 01-02-02, 01-02-01; 02-03-02-22, 02-03-02-23, 02-03-02-24.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, NERC, EPA 625/6-74-003, Washington, 1974, p. 270. 204 Taras, M.J., "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th ed., Method 224A, 1971, p. 535. B) BACKGROUND INFORMATION 532 Howard, C.S., "Determination of Total Dissolved Solids in Water Analysis," <i>Ind. Eng. Chem., Anal. Ed.</i>, 5, 4 (1933). 533 Sokoloff, V.P., "Water of Crystallization in Total Solids of Water Analysis," <i>Ind. Eng. Chem., Anal. Ed.</i>, 5, 336 (1933). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL DISSOLVED (FILTERABLE) SOLIDS		2. IDENTIFICATION CODE 02-03-02-22
3. ABSTRACT OF METHODOLOGY		
To determine total dissolved (filterable) solids, the sample is filtered through a standard glass fiber filter. The filtrate is evaporated to dryness (and constant weight) in a pre-weighed dish at 180°C in an oven. The increase in weight represents total dissolved or filterable solids and includes all materials (liquids and solids) which pass through the filter and are not volatilized during the drying process.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Samples containing high concentrations of calcium, magnesium, chloride, sulfate, and bicarbonate will require prolonged drying, desiccation and rapid weighing. Maximum total residue should be less than 200 mg to prevent encrustation and water entrapment. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE 10-20,000 mg/l filterable solids. B) ACCURACY N/Q C) PRECISION A synthetic sample containing 134 mg/l filterable residue was determined with a standard deviation of ± 13 mg/l in 18 laboratories (using a drying temperature of 103-105°C).		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
N/A		Glass fiber filter discs, filter holder, suction flask, Gooch crucibles, evaporating dishes, steam bath, drying oven, desiccator, analytical balance.
8. KEYWORD INDEX: Total dissolved solids, total filterable solids, aqueous effluents, glass fiber filtration.		
9. CROSS REFERENCE ID NUMBERS 01-02-02, 01-02-01; 02-03-02-21, 02-03-02-23, 02-03-02-24.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 266. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 224E, p. 539. B) BACKGROUND INFORMATION 534 Chanin, G., R.B. Alexander, E.H. Chow and J. Powers, "Use of Glass Fiber Filter Medium in the Suspended Solids Determination," Sewage and Ind. Wastes, 30, 1062 (1958). 535 Wychoff, B.M., "Rapid Solids Determination Using Glass Fiber Filters," Water and Sewage Works, 111, 277 (1964). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL SUSPENDED (NON FILTERABLE) SOLIDS		2. IDENTIFICATION CODE 02-03-02-23
3. ABSTRACT OF METHODOLOGY		
The sample is filtered through a pre-weighed standard glass fiber filter. The filter and residue are dried to constant weight in an oven at 103-105°C. The increase in weight of the filter represents the total suspended (nonfilterable) residue. The filtrate from this method may be used in a determination of total dissolved (filterable) solids (see 02-06-01-02).		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS The quantity of residue on the filter should be minimized in order to prevent encrustation and entrapment of water. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE 10-20,000 mg/l suspended solids. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
N/A		Glass fiber filter discs, filter holders, suction flask, Gooch crucibles, drying oven, desiccator, analytical balance.
8. KEYWORD INDEX: Total suspended solids, total nonfilterable solids, aqueous effluent, glass fiber filtration.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02, 02-03-02-21, 02-03-02-22, 02-03-02-24.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 268. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 224C, p. 537. B) BACKGROUND INFORMATION 536 Degen, J., and F.F. Nussberger, "Notes on the Determination of Suspended Solids," <i>Sewage and Ind. Wastes</i>, 28, 237 (1956). 537 Nusbaum, I., "New Method for Determination of Suspended Solids," <i>Sewage and Ind. Wastes</i>, 30, 1066 (1958). 538 Smith, A.L., and A.E. Greenberg, "Evaluation of Methods for Determining Suspended Solids in Wastewater," <i>J. Water Pollut. Control Fed.</i>, 35, 940 (1963). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF TOTAL VOLATILE SOLIDS	2. IDENTIFICATION CODE 02-03-02-24
3. ABSTRACT OF METHODOLOGY	
To determine total volatile solids, the residue obtained from the determination of total dissolved (filterable) solids (02-03-02-21) or from the determination of total suspended (nonfilterable) solids (02-03-02-23) is ignited at 550°C in a muffle furnace. The loss in weight is then reported as mg/liter volatile residue. This procedure also gives an estimate of the amount of organic matter which is present in the solid fraction of the sample.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to sewage, activated sludge, industrial wastes and bottom sediments. B) INTERFERENCES/LIMITATIONS The method is subject to errors from the following sources: loss of water of crystallization; loss of volatile organic matter prior to combustion; incomplete oxidation of complex organic substances; and decomposition of mineral salts during combustion. C) RECOMMENDED USE AREA Compliance testing.	
5. OPERATIONAL PARAMETERS	
A) RANGE 10-20,000 mg/l solids. B) ACCURACY N/Q C) PRECISION A study of four samples using ten replicates in three laboratories gave a standard deviation of ± 11 mg/l at 170 mg/l volatile residue concentration.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
N/A	Muffle furnace (to 550°C), analytical balance.
8. KEYWORD INDEX: Total volatile solids, aqueous effluents, muffle furnace ashing.	
9. CROSS REFERENCE ID NUMBERS 02-03-02-21, 02-03-02-23; 01-02-01, 01-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 272. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 224B, p. 536. B) BACKGROUND INFORMATION 539 Symons, G.E., and B. Morey, "The Effect of Drying Time on the Determination of Solids in Sewage and Sewage Sludges," <i>Sewage Works J.</i>, 13, 936 (1941). 540 Howard, C.S., "Determination of Total Dissolved Solids in Water Analysis," <i>Ind. Eng. Chem., Anal. Ed.</i>, 5, 4 (1933). 533 Sokoloff, V.P., "Water of Crystallization in Total Solids of Water Analysis," <i>Ind. Eng. Chem., Anal. Ed.</i>, 5, 336 (1933). C) FIELD APPLICATIONS	

1. TITLE DETERMINATION OF TOTAL HARDNESS		2. IDENTIFICATION CODE 02-03-02-25
3. ABSTRACT OF METHODOLOGY		
Total hardness is determined by titrating the sample with ethylenediamine tetra-acetic acid in the presence of an indicator buffered at pH 10. Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetra-acetate (Na_2EDTA). The end point of the reaction is detected by means of Calmagite Indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Certain metal ions (Al^{+3}, Ba^{+2}, Cd^{+2}, Pb^{+2}) interfere but can be removed by the addition of various masking agents such as CN^-. Suspended or colloidal organic matter may interfere, but can be removed by evaporation of a sample aliquot on a steam bath followed by heating in a muffle furnace to 550°C. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is suitable for all hardness concentrations. To avoid large titration volumes, sample aliquots of ~ 25 mg CaCO_3 should be used. B) ACCURACY The analysis of six samples in 19 laboratories gave accuracies (as mg/liter CaCO_3) ranging from -0.003 to -14.3 for samples having 31 to 444 mg/liter hardness as CaCO_3. C) PRECISION Precisions obtained on the above analyses ranged from 2.52 to 9.65 mg/liter as CaCO_3.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Ammonia buffer, inhibitor solutions, Eriochrome Black T, sodium salt of EDTA.		Standard titration apparatus, evaporating dish, muffle furnace (optional).
8. KEYWORD INDEX: Total hardness, calcium and magnesium, aqueous effluents, titrimetry.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-02-01-12.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 68. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 122B, p. 179. B) BACKGROUND INFORMATION 541 Barnard, A.J., Jr., W.C. Broad, and H. Flaschka, "The EDTA Titration," <i>Chemist Analyst</i>, 45, 86 (1956) and 46, 46 (1957). 542 Connors, J.J., "Advances in Chemical and Colorimetric Methods," <i>J. Am. Water Work Assoc.</i>, 42, 33 (1950). 543 Schwarzenbach, G., and H. Flaschka, "Complexometric Titrations," 2nd ed., Barnes and Noble, Inc., New York, 1969. C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF COLOR BY SPECTROPHOTOMETRIC METHOD		2. IDENTIFICATION CODE 02-03-02-26
3. ABSTRACT OF METHODOLOGY		
Method involves measurement of the visible absorption spectrum (percent transmittance) of the sample on a spectrophotometer. The transmittance values corresponding to the wavelengths shown in Columns X, Y and Z of Table are then tabulated and the totals are multiplied by the appropriate factors to obtain tristimulus values, X, Y and Z. The tristimulus value Y is the percent luminance of the waste. Next, the trichromatic coefficients X and Y are calculated using the equations: $X = \frac{X}{X + Y + Z}, Y = \frac{Y}{X + Y + Z}$ Then, the point (X, Y) is located on one of the chromaticity diagrams in Figure and the dominant wavelength (in mμ) and purity (in percent) are determined. The hue is determined from the dominant wavelength as indicated in Table. Since the method is pH dependent, two samples are determined simultaneously, one at the original pH, and one having pH of 7.6 from the addition of sulfuric acid and sodium hydroxide.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Turbidity interferes; this can be eliminated by sample centrifuging and filtration. The determination should be performed as soon as possible on the collected sample, which should be refrigerated at 4°C to retard biological activity. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is applicable to all colored wastes, including highly colored industrial wastes which cannot be determined by the platinum-cobalt method (02-02-01-35). B) ACCURACY Not available. C) PRECISION Not available.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Concentrated sulfuric acid, sodium hydroxide.	Spectrophotometer, pH meter, centrifuge, filter funnel, standard laboratory glassware.	
8. KEYWORD INDEX: Color, aqueous effluents, spectrophotometry.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-03-02-27.		
10. REFERENCES		
A) PRIMARY SOURCE 185 "Methods for Chemical Analysis of Water and Wastes", Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 39. 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 206A, p. 392. B) BACKGROUND INFORMATION 544 Hardy, A.C., "Handbook of Colorimetry," Technology Press, Boston, Mass., 1936. 545 Rudolphs, W., and W.D. Hanlon, "Color in Industrial Wastes I. Determination by Spectrophotometric Method," <u>Sewage and Ind. Wastes</u>, 23, 1125 (1951). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF COLOR BY PLATINUM-COBALT METHOD		2. IDENTIFICATION CODE 02-03-02-27
3. ABSTRACT OF METHODOLOGY		
Method involves visual comparison of the sample with platinum-cobalt standards. The color of the solution is measured in units; one unit of color is the color produced by 1 mg/l platinum as chloroplatinate ion. The stock standard solution, which has a color of 500 units, is prepared by dissolving 1.246 g potassium chloroplatinate and 1.00 g cobaltous chloride in 100 ml HCl and diluting to 1000 ml. Standards having color units of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, and 70 are then prepared from the stock solution. The color of the sample (or sample aliquot) is then matched to that of the standards.		
4. APPLICATION: Compliance, environmental assessment.		
A) OPERATIONAL SCOPE Method is applicable to all aqueous streams except highly colored industrial wastes. B) INTERFERENCES/LIMITATIONS Visible turbidity interferes; this can be removed by centrifugation. Since the method is pH dependent, the pH of the sample should be recorded. C) RECOMMENDED USE AREA Compliance testing.		
5. OPERATIONAL PARAMETERS		
A) RANGE Method is applicable to all samples except highly colored industrial wastes; the sample can be diluted until its color is within the range of the standards. B) ACCURACY Not available at this time. C) PRECISION Not available at this time.		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Potassium chloroplatinate, cobaltous chloride, concentrated hydrochloric acid.	Matched Nessler tubes, pH meter, standard laboratory glassware.	
8. KEYWORD INDEX: Color, aqueous effluents, colorimetry, platinum-cobalt method.		
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02; 02-03-02-26.		
10. REFERENCES		
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 118, p. 160. 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 36. B) BACKGROUND INFORMATION 546 Knight, A.G., "The Photometric Estimation of Color in Turbid Waters," <u>J. Inst. Water Eng.</u>, 5, 623 (1951). 547 Jullander, I., and K. Brune, "Light Absorption Measurements on Turbid Solutions," <u>Acta. Chem. Scandinav.</u>, 4, 870 (1950). 548 Lamar, W.L., "Determination of Color of Turbid Waters," <u>Anal. Chem.</u>, 21, 726 (1949). 549 Block, A.P., and R.F. Chrestman, "Characteristics of Colored Surface Waters," <u>J. Am. Water Works Assoc.</u>, 55, 753 (1963). 550 Rudolphs, W., and W.D. Hanlon, "Color in Industrial Wastes," <u>Sewage and Ind. Wastes</u>, 23, 1125 (1951). C) FIELD APPLICATIONS		

1. TITLE DETERMINATION OF SPECIFIC CONDUCTANCE	2. IDENTIFICATION CODE 02-03-02-28
3. ABSTRACT OF METHODOLOGY The specific conductance of a sample is determined by measurement of electrical resistance or its inverse, conductance, between two electrodes one centimeter apart. A specific conductance cell, a Wheatstone bridge and a source of electric current, or a self-contained conductance cell, are used to measure the electrical resistances of a sample and a potassium chloride solution of known specific conductance. Since the method is temperature dependent, a water bath is used to maintain the samples at 25°C.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. B) INTERFERENCES/LIMITATIONS Samples should be protected from exposure to ammonia or acidic gases before measurement; also, samples should be protected from absorption or desorption of dissolved gases. C) RECOMMENDED USE AREA Compliance testing.	
5. OPERATIONAL PARAMETERS	
A) RANGE Suitable for use on all aqueous samples B) ACCURACY Analyses in 17 laboratories of six synthetic samples containing increments (as specific conductance) of 100 to 1710 $\mu\text{mho/cm}$ gave accuracies as percent bias from -0.76 to -5.36. C) PRECISION The determinations on the samples described above gave precisions ranging from 7.55 to 119 $\mu\text{mho/cm}$. In a single laboratory using samples with an average conductivity of 536 $\mu\text{mho/cm}$, a standard deviation of ± 6 was obtained.	
6. REAGENTS REQUIRED Potassium chloride, reagent grade water, platinizing solution (chloroplatinic acid, lead acetate) hydrochloric acid.	7. EQUIPMENT REQUIRED Specific conductance cell, Wheatstone bridge, source of electric current, water bath (25°C), standard laboratory glassware.
8. KEYWORD INDEX: Specific conductance, aqueous effluents, conductivity meter.	
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-02.	
10. REFERENCES	
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 154, p. 323. 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, p. 275. 024 ASTM Committee D-19 and D-22, "Water; Atmospheric Analysis," 1971 Annual Book of ASTM Standards, Part 23, D1125-64, "Standard Methods of Test for Electrical Conductivity of Water," American Society for Testing and Materials, Philadelphia, PA., 1971, pp. 156-161. B) BACKGROUND INFORMATION 551 Robinson, R.A., and R.H. Stokes, "Electrolyte Solutions," 2nd ed., Academic Press, New York, N.Y., 1959, p. 466. 552 Lind, J.E., R.M. Fuoss and J.J. Zwolenik, "Calibration of Conductance Cells at 25°C with Aqueous Solutions of Potassium Chloride," <i>J. Am. Chem. Soc.</i>, 81, 1557 (1959).	

TITLE

DETERMINATION OF SPECIFIC CONDUCTANCE (CONTINUED)

ID NO.

02-03-02-28

C) FIELD APPLICATIONS

- 553 Jones, G., and B.C. Bradshaw, "The Measurement of the Conductance of Electrolytes. V. A Redetermination of the Conductance of Standard Potassium Chloride Solutions in Absolute Units," J. Amer. Chem. Soc., 55, 1780 (1933).
- 554 Rossum, J.R., "Conductance Method for Checking Accuracy of Water Analyses," Anal. Chem., 21, 631 (1949).
- 555 Wilcox, L.V., "Electrical Conductivity," J. Am. Water Works Assoc., 42, 775 (1950).

1. TITLE DETERMINATION OF TURBIDITY BY THE NEPHELOMETRIC METHOD	2. IDENTIFICATION CODE 02-03-02-29
3. ABSTRACT OF METHODOLOGY	
A turbidimeter is used to measure the intensity of light scattered by a sample, compared to that scattered by a standard reference suspension. The turbidimeter consists of a nephelometer having a light source, one or more photoelectric detectors, and a readout device which indicates the light intensity scattered at right angles to the incident beam. Readings are recorded in nephelometric turbidity units (NTU's). A standard polymer solution (hydrazine sulfate or hexamethylenetetramine) is used as a reference suspension for instrument calibration.	
4. APPLICATION: Compliance, environmental assessment.	
A) OPERATIONAL SCOPE Method is applicable to domestic, surface and saline waters. B) INTERFERENCES/LIMITATIONS Samples should be determined as soon as possible, since sediment will settle out and give low readings. Air or gas bubbles will give high results. Excessive solution color will result in low values. C) RECOMMENDED USE AREA Compliance testing.	
5. OPERATIONAL PARAMETERS	
A) RANGE Suitable for use on all aqueous samples in the range of 0 to 40 nephelometric turbidity units. B) ACCURACY Not available at this time. C) PRECISION Standard deviations of ± 0.60, ± 0.94, ± 1.2 and ± 4.7 units were obtained in a single laboratory using surface water samples at levels of 26, 41, 75 and 180 NTU.	
6. REAGENTS REQUIRED Turbidity-free water, standard turbidity suspension (hydrazine sulfate or hexamethylenetetramine).	7. EQUIPMENT REQUIRED Turbidimeter (such as Hach Model 2100 turbidimeter), 0.45 μ pore size membrane filter, standard laboratory glassware, analytical balance.
8. KEYWORD INDEX: Turbidity, aqueous effluents, nephelometry.	
9. CROSS REFERENCE ID NUMBERS 01-02-01, 01-02-07.	
10. REFERENCES	
A) PRIMARY SOURCE 204 Taras, M.J. (ed.), "Standard Methods for the Examination of Water and Wastewater," 13th ed., American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Washington, D.C., 1971, Method 163A, p. 349. 185 "Methods for Chemical Analysis of Water and Wastes," Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, EPA 625/6-74-003, Washington, 1974, Page 295. B) BACKGROUND INFORMATION 556 Knight, H.G., "The Measurement of Turbidity in Water," <u>J. Inst. Water Eng.</u>, 5, 633 (1951). 557 Packham, R.F., "The Preparation of Turbidity Standards," <u>Proc. Soc. Water Treatment and Exam.</u>, 11, 64 (1962). 558 Eden, G.E., "The Measurement of Turbidity in Water. A Progress Report on the Work of the Analytical Panel," <u>Proc. Soc. Water Treatment and Exam.</u>, 14, 27 (1965). C) FIELD APPLICATIONS 559 Black, A.P., and S.A. Hannah, "Measurement of Low Turbidities," <u>J. Am. Water Works Assoc.</u>, 57, 901 (1965).	

1. TITLE VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES	2. IDENTIFICATION CODE 02-03-02-30
3. ABSTRACT OF METHODOLOGY	
Method involves the visual determination of the relative opacity of an emission (usually a plume) by a qualified observer using a Ringelmann smoke card. The determination of plume opacity involves the minimization of certain variables which may influence the appearance of the plume but which may be controlled. These include: (1) angle of the observer with respect to the plume; (2) point of observation of attached and detached steam plume; and (3) angle of the observer with respect to the plume emitted from a rectangular stack with a large length-to-width ratio. Other variables which may not be controllable are luminescence and color contrast between the plume and the background against which the plume is viewed.	
4. APPLICATION: Compliance.	
A) OPERATIONAL SCOPE Method is applicable to the determination of the relative opacity of visible emissions from stationary sources. B) INTERFERENCES/LIMITATIONS Positive bias may result when the plume is viewed under maximum contrasting conditions. Negative bias can be obtained when the plume is viewed under less contrasting conditions. C) RECOMMENDED USE AREA Compliance testing.	
5. OPERATIONAL PARAMETERS	
A) RANGE Method can be used to measure any range of plume opacity. B) ACCURACY N/Q C) PRECISION ±5% or better.	
6. REAGENTS REQUIRED Not applicable.	7. EQUIPMENT REQUIRED Smoke meter, including light source and photo cell.
8. KEYWORD INDEX: Opacity, Stationary Sources, Compliance.	
9. CROSS REFERENCE ID NUMBERS 01-01; 01-05.	
10. REFERENCES	
A) PRIMARY SOURCE 560 U.S. Environmental Protection Agency. "Visual Determination of the Opacity of Emissions from Stationary Sources," Federal Register 36, No. 247, 24895, Dec. 23, 1971. B) BACKGROUND INFORMATION 561 Air Pollution Control District Rules and Regulations, Los Angeles County, Air Pollution Control District, Chapter 2, Schedule 6, Regulation 4, Prohibitions, Rule 50, 17 pp. 562 Kudluk, R., "Ringelmann Smoke Chart," U.S. Dept. of Interior, Bureau of Mines, Information Circular No. 8333, May 1967. 563 Weisburd, M.I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, N.C., APTD-1100, Aug. 1972, p. 4.1-4.36. C) FIELD APPLICATIONS	

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(EDX)

APPLICATION MATRIX FOR 02-04 SOLID AND PARTICULATE COMPOUND ANALYSIS

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
02-04-01-01	●		
02-04-01-02			●
02-04-01-03			●
02-04-01-04			●
02-04-02-01			●
02-04-02-02			●
02-04-02-03			●

SOLID AND PARTICULATE COMPOUND ANALYSIS - ID No. 02-04

A variety of instruments are available for the analysis of solids and particulate matter for morphological characteristics and compound analysis. Analyses are routinely performed by scanning electron microscopy, electron probe microanalysis, transmission electron microscopy, X-ray diffraction, electron spectroscopy, and polarized light microscopy. They can be used to determine a wide range of morphological characteristics, such as size, shape, and size frequencies of the particles. These instruments are non-destructive, allow multiple studies on single specimens, and are generally characterized by high spatial resolution. A summary of these techniques, the detectable particle sizes and principal information derived are shown in Table 02-04A.

02-04-01 Microscopic Analysis (Abstracts 02-04-01-01 Through 02-04-01-04)

Light microscopy (02-04-01-01) is routinely used for physical inspection of samples, particularly as a means of quality control for verification of the physical integrity of the sample. Light microscope techniques measure incident and transmitted light and employ bright field, dark field, polarized light and phase contrast techniques to identify specimens. Most common minerals (or compounds) as small as 10μ can be identified.

One of the principal tools for analytical and morphological determinations is the Scanning Electron Microscope (SEM) (02-04-01-04). Quantitative (references 344, 345, 347, 355) analysis of particles as small as 0.1μ for morphological and elemental composition is possible when an energy-dispersive detector is used. Characteristic X-ray emissions can be obtained from elements of atomic number 11, while elemental content of 1% by weight can be routinely determined.

In the identification of fiber-like particles such as asbestos, Transmission Electron Microscopy (TEM) (02-04-01-02) is preferred to SEM and EPMA techniques. This is because: 1) smaller fibers can be observed and identified by TEM, and 2) TEM using selected area electron diffraction is more dependable for elemental analysis of particles. TEM

Technique	Detectable Particle Size	Principal Information Derived	Method of Identification
Polarized Light Microscopy (PLM)	5 to 10 μ	Structural parameters; general sample integrity	Imaging techniques using incident and transmitted light
Transmission Electron Microscopy (TEM)	0.01-1 μ	Particle size distributions	Detection of transmitted electron beam
Scanning Electron Microscopy (SEM)	0.1 to 100 μ	Surface microstructure	Detection of secondary electron beam
Electron Probe Microanalysis (EPMA)	1 μ and larger	Morphological parameters; elemental distribution	Detection of emitted X-rays; compound identification by ratio of elements
Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX)	>0.1 μ	Elemental ratios for individual particles	Compound identification by ratio of known elements
X-Ray Diffraction (XRD)	>10 μ	Direct determination of crystalline compounds present	By diffraction pattern of crystalline material
Electron Spectroscopy for Chemical Analysis (ESCA)	-	Direct compound analysis	By characteristic chemical shift of photoelectron spectra

Table 02-04-A. Morphological and Compound Characterization Techniques.

(reference 346) analyses are generally reliable even when the collected particles are small in number compared to background particles because a unique system of blank determination. TEM has been used to examine particles ranging from 0.01 to 1 micron in size.

Electron Probe Microanalysis (EPMA) (02-04-01-03) is particularly useful for obtaining compositional information, and a spatial resolution of 1 μ m can be obtained for a sample. EPMA (reference 350) which is equipped with an Energy Dispersive Spectrometer (reference 350) can rapidly determine all elements with an atomic number greater than 11. X-ray imaging systems are particularly useful by providing a visual map of elemental distributions. Wavelength dispersive crystal spectrometers are also available for quantitative analyses, and can determine characteristic X-ray emissions from elements with atomic numbers of 6 or greater. Routine precisions of $\pm 1\%$ can be attained; even more precise results are obtained when standards are available which closely match the specimen being analyzed.

02-04-02 Chemical Analysis (Abstracts 02-04-02-01 Through 02-04-02-03)

Qualitative and quantitative chemical analyses are routinely performed using SEM and EPMA (02-04-02-03) techniques, particularly when they are coupled to energy dispersive spectrometers. These techniques have been used to measure the distributions of Zn, Cu and Fe in mud samples; the Ag, S, and Si distribution in ores, and the Cu and Zn content of brass samples. The composition of fly ash also is routinely determined. Quantitative chemical analysis is based on one or more computational schemes which convert the x-ray intensity ratios to the chemical composition of the sample.

X-ray Diffraction (XRD) (02-04-02-01) provides a rapid method for qualitative and semiquantitative determination of solids and particulates, and yields compound information to compliment the morphological and elemental information supplied by SEM, EPMA and TEM. Materials such as lime, calcium carbonate, road salt, coke dust and aerosol from sinter emissions as well as particulate samples obtained from dustfall or high volume filter media are easily determined (references 351, 352, 353, 354). The components of a sample may be identified by matching the diffraction pattern obtained from a particle with known ASTM patterns. Internal standards, such as calcium carbonate, kaolin or powdered amorphous glass are also used.

Unlike SEM, EPMA and TEM, Electron Spectroscopy for Chemical Analysis (ESCA) (02-04-02-02) performs direct compound identification. ESCA techniques can be used to qualitatively identify all elements present in a sample, with the exception of hydrogen, and is also used in compound identification (references 349, 356). ESCA measures the energy of the photoelectrons ejected from a sample under bombardment by monoenergetic X-rays. Minute shifts in the energy of the photoelectrons from the same element but in different compounds identify the element's origin (compound). Since peak areas are proportional to the concentrations of the corresponding elements in a sample, calibration curves are used in quantitative compound analysis. ESCA techniques have been used in the determination of small molecules, such as carbon monoxide, nitrogen, methane, and in the identification of larger organic compounds (organophosphorous compounds, mercury-containing compounds, fluoromethane gases). Recently (reference 356) ESCA was used to measure the kind and quantity of sulfur and nitrogen compounds present in an atmospheric aerosol.

REFERENCES

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- 347 Griffiths, B.W., "Analytical Scanning Electron Microscopy," Am. Lab., April 1974, p. 83.
- 348 Brundle, C.R., "Some Recent Advances in Photoelectron Spectroscopy," Appl. Spect., 25(1), 8, 1971.
- 349 Betteridge, D., "Analytical Aspects of Photoelectron Spectroscopy," Intern. J. Envir. Anal. Chem., 1, 243-57 (1972).
- 350 Performance Evaluation of an Ion Microprobe, Applied Research Laboratories brochure, P.O. Box 129, Sunland, CA., September 1971.
- 351 Richards, A.L., "Estimation of Trace Amounts of Chrysotile Asbestos by X-Ray Diffraction," Anal. Chem., 44(11), 1872, September 1972.
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- 353 Warner, P.O., J.O. Jackson and L. Saod, "Identification and Quantitative Analysis of Particulate Air Contaminants by X-Ray Diffraction Spectrometry," Air Pollution Control Association, 64th Annual Meeting, Atlantic City, N. J., June 27-July 2, 1971.
- 354 Baldock, P.J., and A. Parker, "X-Ray Powder Diffractometry of Small (20 μ g to 1 μ g) Samples Using Standard Equipment," J. Appl. Cryst., 6, 153 (1973).
- 355 Waller, R.E., A.G.F. Brooks and J. Cartwright, "An Electron Microscopy Study of Particles in Town Air," Int. J. Air Water Poll., 7, 779-786.
- 356 Novakov, T., et al, "Aerosols and Atmospheric Chemistry," G.M. Hidy (ed.), Academic Press, N. Y., 1972, p. 285.

1. TITLE POLARIZED LIGHT MICROSCOPE IDENTIFICATION OF AIR PARTICULATE		2. IDENTIFICATION CODE 02-04-01-01
3. ABSTRACT OF METHODOLOGY		
Polarized light is used to view particles collected from various sources. Particles are first crushed to 0.05 mm and then examined with the microscope. Figure 02-04-01-01A, which is taken from the primary reference, describes the steps leading to particle identification. Of special importance are the observations of refractive index, (relief) isotropy or anisotropy, birefringence, pleochroism, fracture, color, and crystal habit.		
4. APPLICATION: Environmental assessment.		
A) OPERATIONAL SCOPE This method can be used to identify collected particulates from filters, cyclones, or impactors. Crystalline materials are best suited for study, though many substances can be identified by observation of morphological properties (see Ref. 359). B) INTERFERENCES/LIMITATIONS Polarized light microscopy is limited to single particle analysis. Trace constituents absorbed on particles or extremely small particles (<0.5 μ) must be measured by another technique (SEM - EDX). Homogeneity is important for correct identification. C) RECOMMENDED USE AREA Level 1 environmental assessment quality control and preliminary screening.		
5. OPERATIONAL PARAMETERS		
A) RANGE Particles > 0.5 μ, major components. B) ACCURACY N/Q (if particles are homogeneous, ± 5 estimated). C) PRECISION N/Q		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Shellabro's Oil.	Petrographic microscope, microscope slides, cover glasses.	
8. KEYWORD INDEX: Analysis, polarized light microscopy.		
9. CROSS REFERENCE ID NUMBERS 01-06-01, 02; 01-04-01, 02.		
10. REFERENCES		
A) PRIMARY SOURCE 357 West, P.W., <i>The Chemist Analyst</i>, 34, 76 (1945). 358 West, P.W., <i>The Chemist Analyst</i>, 35, 28 (1946). B) BACKGROUND INFORMATION 359 McCrone, W.C. (ed.), "The Particle Atlas," Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1967. 360 Chamot, E.M., and C.W. Mason, "Handbook of Chemical Microscopy," New York, John Wiley and Sons Inc., 2nd ed., 1939, 2 volumes. C) FIELD APPLICATIONS		

TITLE POLARIZED LIGHT MICROSCOPE IDENTIFICATION OF AIR PARTICULATE (CONTINUED)

ID NO. 02-04-01-01

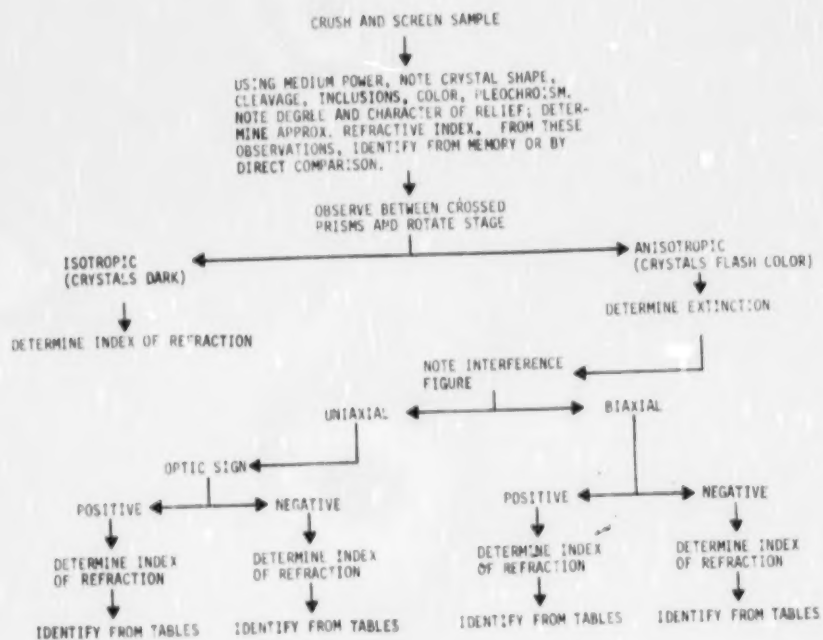


Figure 02-04-01-01A. From West, P.W., The Chemist Analyst, 34, 76 (1945).

1. TITLE QUANTITATIVE ANALYSIS USING TRANSMISSION ELECTRON MICROSCOPY (TEM)		2. IDENTIFICATION CODE 02-04-01-02
3. ABSTRACT OF METHODOLOGY		
TEM involves the impingement of an electron beam on a thin film of sample. The resultant transmitted electron beam is observed and recorded. Quantitative analysis using TEM is superior to SEM (02-04-01-04) because: a) smaller samples can be observed and identified using TEM, and b) the selected area electron diffraction (SAED) is generally more dependable for identification of chemical species such as asbestos than the elemental analysis capabilities of SEM. Sample preparation involves collection of sample on a membrane filter; a section of the filter is then placed on a carbon-coated electron microscope grid, and the filter is then dissolved using acetone in a Soxhlet extractor. Subsequent mass, density and size distribution can be achieved. Combinations of TEM and EPMA (see 02-04-01-04) allow even greater resolution, with subsequent identification by diffraction pattern and elemental analysis.		
4. APPLICATION: Engineering evaluation R&D		
A) OPERATIONAL SCOPE Method is applicable to analysis of particulates collected from flue gas and fugitive emissions. B) INTERFERENCES/LIMITATIONS N/Q C) RECOMMENDED USE AREA TEM is one of the approaches usable for compound analysis.		
5. OPERATIONAL PARAMETERS		
A) RANGE Measurement range of angstroms can be obtained. B) ACCURACY N/Q C) PRECISION N/A		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
N/A	Transmission electron microscope; EPMA apparatus (optional).	
8. KEYWORD INDEX: Transmission electron microscope, particulates, quantitative analysis, asbestos.		
9. CROSS REFERENCE ID NUMBERS 01-04; 01-06; 02-04-01-04, 02-04-01-04.		
10. REFERENCES		
A) PRIMARY SOURCE 361 McCrone, W.C., and I.M. Stewart, "Asbestos," <u>American Laboratory</u>, p. 13-18, April 1974. B) BACKGROUND INFORMATION 362 Goldstein, J.I., and H. Yakowitz, "Practical Scanning Electron Microscopy," New York, Plenum Press, 1975, p. 44. C) FIELD APPLICATIONS 363 Yakowitz, H., et al., "Analysis of Urban Particulates by Means of Combined Electron Microscopy and X-Ray Microanalysis," <u>Micron</u>, <u>3</u>, 506-525 (1972).		

1. TITLE ELECTRON PROBE MICROANALYSIS (EPMA) FOR PARTICULATE ANALYSIS	2. IDENTIFICATION CODE 02-04-01-03
3. ABSTRACT OF METHODOLOGY	
EPMA (or electron microprobe) can be used in qualitative and quantitative determination of elements above atomic number 6. A small energetic electron beam impinges the surface of the specimen and causes characteristic X-ray emissions which are subsequently analyzed by wavelength dispersion techniques (see 02-04-02-03). The X-ray output consists of spectral probes at characteristic wavelengths; the positions of the wavelengths are used for qualitative analysis. For quantitative analysis, the peak heights (intensity ratios) are measured on both the unknown and a standard of known composition. Chemical species in urban particulates mounted on carbon films or copper grids have been semi-quantitatively analyzed using EPMA techniques (See Reference 368). Trace elements (Ti, V, Cr, Mn, Co, Cu, Ni and Zn) in silicates have also been determined (See Reference 362).	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to analysis of particulates collected from flue gas samples, fugitive emissions. This method is intended for single particle chemical analysis. B) INTERFERENCES/LIMITATIONS Interferences may arise from the excitation of small surface contaminant particles lying atop larger particles. The use of standards whose composition closely matches the specimen being analyzed gives better results than analyses performed without standards. C) RECOMMENDED USE AREA This method is applicable to compound identification of single particles on homogeneous bulk samples.	
5. OPERATIONAL PARAMETERS	
A) RANGE For 15 kV operation, minimum detectability limits are 200 $\pm$100 ppm for Ti; 450 $\pm$200 ppm for Zn; particles of $<0.5 \mu\text{m}$ in diameter can be analyzed; sensitivities of 1/10% to 1/100% can be attained. B) ACCURACY 99% confidence levels can be achieved. C) PRECISION Values obtained by EPMA can fall within one standard deviation of the calibration curves for elemental NBS standards.	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED EPMA microprobe, typically operated at 15 to 20 kV and specimen currents of 2×10^{-8} amperes.
8. KEYWORD INDEX: Electron probe, microanalyses, particulates, quantitative analysis, silicates.	
9. CROSS REFERENCE ID NUMBERS 01-04; 01-06; 02-04-01-04; 02-04-02-03.	
10. REFERENCES	
A) PRIMARY SOURCE (See Continuation Sheet) B) BACKGROUND INFORMATION (See Continuation Sheet) C) FIELD APPLICATIONS (See Continuation Sheet)	

TITLE ELECTRON PROBE MICROANALYSIS (EPMA) FOR PARTICULATE ANALYSIS (CONTINUED)

ID NO. 02 04 01 03

A) PRIMARY SOURCE

- 364 Heidel, R.H., and G.A. Desborough, "Precision and Detection Limits of Certain Minor and Trace Elements in Silicates by Electron Microprobe Analysis," in "Proceedings of the 6th National Conference on Electron Probe Analysis," Pittsburgh, PA., (July 27-30, 1971), p. 25 A-B.
- 365 "Advances in X-Ray Analysis," Volume 15, K.F.J. Heinrich (ed.), New York, Plenum Press, 1972, p. 150.

B) BACKGROUND INFORMATION

- 362 Goldstein, J.I., and H. Yakowitz, "Practical Scanning Electron Microscopy," New York, Plenum Press, 1975, p. 1 and p. 230.
- 366 "Quantitative Electron Probe Microanalysis," National Bureau of Standards Special Publication 298, Washington, October 1968.
- 367 DeHoff, R.T., and F.N. Rhines, "Quantitative Microscopy," New York, McGraw-Hill, 1968.

C) FIELD APPLICATIONS

- 237 Birks, L.S., "X-Ray Spectrochemical Analysis," Interscience Publishers, Inc., New York, 1959.
- 368 Yakowitz, H., et al., "Analysis of Urban Particulates by Means of Combined Electron Microscopy and X-ray Microanalysis," Micron, 1, 506-525 (1972).

1. TITLE SCANNING ELECTRON MICROSCOPY (SEM) FOR QUALITATIVE PARTICULATE ANALYSIS	2. IDENTIFICATION CODE 02-04-01-04
3. ABSTRACT OF METHODOLOGY	
In scanning electron microscopy (SEM), the specimen is swept by an electron beam, and the variation of the secondary electron emission intensity is recorded by a secondary electron detector. The signal simultaneously modulates the brightness of an oscilloscope beam, producing an image on the surface of the oscilloscope screen. Since the secondary electron beam is localized in the beam impact area, images of relatively high resolution are achieved. Morphological characteristics of the specimen are then determined from the generated images. Some applications of SEM include analysis of small particles from ball bearings for Fe, Si, K, Zn, the determination of percentage of oxides and sulfides in steel, silicates in wrought iron, and carbides in steel. (See 02-04-02-03 and Reference 362.) Combinations of SEM and EPMA techniques (see 02-04-02-03) yield qualitative and semiquantitative data. The SEM-EPMA approach involves dispersal of sample (particulates) on a suitable substrate (germanium) with subsequent scanning in raster form. When a monitor on the secondary electron signal indicates that the electron beam has encountered a particle, the beam is stopped, and a scan is also measured, and is related to the mass thickness of the sample. The accumulated data yield detailed information on particle size, shape, mass distribution and tentative composition. (See Reference 372.)	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to analysis of particulates from flue gas sampling, fugitive emissions, and solid samples. B) INTERFERENCES/LIMITATIONS Interferences may arise from excitation of small surface contaminant particles lying atop larger particles. This is essentially a surface technique. C) RECOMMENDED USE AREA This method can be used to identify a particle by its morphological characteristics.	
5. OPERATIONAL PARAMETERS	
A) RANGE Measurement range of several angstroms can be achieved, depending upon the resolution of the imaging system. B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED SEM apparatus is comprised of lens system, electron gun, electron collector, visual and recording cathode ray tubes and associated electronic hardware.
8. KEYWORD INDEX: Scanning electron microscopy, electron microprobe analysis, particulates.	
9. CROSS REFERENCE ID NUMBERS 01-04; 01-06; 02-04-01-03; 02-04-02-03.	
10. REFERENCES	
A) PRIMARY SOURCE 362 Goldstein, J.I., and H. Yakowitz, "Practical Scanning Electron Microscopy," New York, Plenum Press, 1975, p. 236. 369 Griffiths, B.N., "Analytical Scanning Electron Microscope," <u>American Laboratory</u>, 83-9, April 1974. B) BACKGROUND INFORMATION 370 "Qualitative Metallurgical Systems (QMS)," Bausch & Lomb, Scientific Instrument Division Brochure, Cat. No. 42-2337, 1071, 19 p. 371 Griffiths, B., A.V. Jones and J. Wardell, "Scanning Electron Microscopy: Systems and Applications," Newcastle, 1973, p. 42-5. 372 "SEM/1973 Proceedings of the 6th Annual SEM Symposium," (D. Johari, ed.), IITRI, Chicago, Ill., 1973, p. 121. C) FIELD APPLICATIONS 373 Goldstein, J.I., E. Henderson and H. Yakowitz, "Proceedings of the Apollo 11 Lunar Science Conference," 1970, Vol. 1, p. 499. 374 Bayard, M., "Microprobe Analysis," (C.A. Andersen, ed.), New York, Wiley, 1973, p. 323. 375 Ruff, Jr., A.W., NBSIR 74-474, 1974, p. 15.	

1. TITLE QUANTITATIVE COMPOUND CHEMICAL ANALYSIS BY X-RAY POWDER DIFFRACTION (XRD)		2. IDENTIFICATION CODE 02-04-02-01
3. ABSTRACT OF METHODOLOGY		
X-Ray powder diffraction involves a powder sample diffracting a primary x-ray beam into a series of diffraction lines which are characteristic of a given crystalline substance. Mineral determinations commonly employ 5 percent internal standard (CaCO_3, kaolin) with subsequent quantification by comparison to standard curves. Microgram quantities of SiO_2 and NaO, dispersed with a diamond grinding paste of appropriate particle size, can be determined using fluorite windows cut parallel to 100 and 410 planes. Quantitative determination of SiO_2 on sized airborne particulates is conducted using CaF_2 of the same size range as the collected sample as the internal standard; the results of the determinations are compared to calibration plots of the intensity of the $\text{CaF}_2/\text{SiO}_2$ line versus weight of $\text{CaF}_2/\text{SiO}_2$. A new technique which eliminates interferences caused by internal standards involves dispersal of the sample (mineral or particulates) in a matrix of finely powdered amorphous glass. (Reference 376)		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE Method is applicable to analysis of crystalline components of particulates from flue gases and fugitive emissions. Solid material can be crushed to less than 2μ and then analyzed by this method. B) INTERFERENCES/LIMITATIONS Major spectral interferences due to use of kaolin, calcium carbonate, etc., are eliminated using amorphous glass as internal standard. Method is not applicable to determination of SO_2 adsorbed on solid such as PbO_2. Amorphous materials are not recorded. C) RECOMMENDED USE AREA This is the recommended engineering evaluation R&D method for the determination of crystalline compounds in particulate matter.		
5. OPERATIONAL PARAMETERS		
A) RANGE Samples of ng to microgram quantities can be determined, depending on the technique employed. B) ACCURACY $\pm 5\%$ using the amorphous glass internal standard $\pm 10\%$ using microgram samples and parallel-cut fluorite windows. C) PRECISION $\pm 10\%$ or better.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Reagents are dependent upon technique used, e.g., powdered amorphous glass, kaolin, calcium carbonate, etc.		X-ray diffraction spectrometer with strip chart recorder; sample preparation equipment (powder mixers, stainless steel balls).
8. KEYWORD INDEX: X-ray diffraction, particulates, quantitative analysis.		
9. CROSS REFERENCE ID NUMBERS 01-04-01-02, 01-04-02-01; 01-06-01-01, 01-06-02-01; 01-05-02-01.		
10. REFERENCES		
A) PRIMARY SOURCE (See reverse side) B) BACKGROUND INFORMATION (See reverse side) C) FIELD APPLICATIONS (See reverse side)		

TITLE QUANTITATIVE COMPOUND CHEMICAL ANALYSIS BY X-RAY POWDER DIFFRACTION
(XRD) (CONTINUED)

ID NO. 02-04-02-01

A) PRIMARY SOURCE

- 376 Warner, P.O., et al, "Identification and Quantitative Analysis of Particulate Air Contaminants by X-Ray Diffraction Spectrometry," presented at 64th Annual Meeting of the Air Pollution Control Association, Atlantic City, N.J., June 27 - July 2, 1971, 15 pp.
- 378 Oberg, M., "Evaluation of Quartz in Airborne Dust in the 0.5- to 2-micron Size Range," *Environ. Sci. Tech.*, 2, (10), 795 (October 1968).
- 379 Baldock, P.J., and A. Parker, "X-Ray Diffractometry of Small (20 μ g to 1 μ g) Samples Using Standard Equipment, *J. Appl. Cryst.*, 9, 153 (1973).

B) BACKGROUND INFORMATION

- 361 McCrone, W.C., and I.M. Stewart, "Asbestos," *Amer. Lab.*, pp. 13-18, April 1974.
- 362 Ewing, G.W., "Instrumental Methods of Chemical Analysis," New York, McGraw-Hill Book Company, Third Edition, 1960, p. 195.

C) FIELD APPLICATIONS

- 381 Waller, R.E., et al, "An Electron Microscope Study of Particles in Town Air," *Int. J. of Air Water Pollut.* Pergamon Press, 1963, Vol. 7, pp. 787-97.
- 382 Johns, W.D., and R.E. Grim, "Quantitative Estimates of Clay Minerals by Diffraction Methods," *Journal of Sedimentary Petrology*, 24, (4), 242-51 (1954).
- 383 Window, R.L., "Atmospheric Dust Records in Permanent Snowfields: Implications to Marine Sedimentation," *Biological Society of America Bulletin*, 80, 761-82 (1969).
- 384 Carl, H.F., "Quantitative Mineral Analysis with a Recording X-Ray Diffraction Spectrometer," *Am Mineralogist*, 32, 508 (1947).
- 385 M. Feldstein, et al, "The Collection and Analysis of Inorganic Dust Downwind of Source Effluents," presented at 61st Annual Meeting of the Air Pollution Control Association, 1968.
- 386 Leroux, J., and C.A. Powers, "Direct X-Ray Diffraction Analysis Quartz in Industrial Films Deposited on Silver Membrane Filters," *Staub-Reinhold*, 29, 26 (1969).
- 387 Talvetie, N.A., and H.W. Brewer, "X-Ray Diffraction Analysis of Industrial Dust," *A.I.H.A.S.*, 23, 214 (1962).

1. TITLE COMPOUND IDENTIFICATION BY ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)		2. IDENTIFICATION CODE 02-04-02-02
3. ABSTRACT METHODOLOGY		
Electron Spectroscopy for Chemical Analysis (ESCA) accurately measures the binding energy of an electron both for elemental characterization and for the measurement of chemical shifts resulting from the atomic environment of each element. The sample is irradiated with X-rays causing inner orbital electrons to be ejected. The energy of these photo-electrons is a measure of the binding energy of the electrons as modified by the chemical surroundings of the emitting atom. Thus energy shifts in the binding energy of electrons emitted from the same element indicate different chemical environments (i.e., compounds). ESCA is extremely surface limited as the electrons have a shallow (3-20 Å) escape depth. This feature makes ESCA an extremely useful tool to study adsorption phenomena such as SO₂ or soot or fly ash. Most commercial instruments have ion beam sputtering for sequential removal of atomic layers. Quantization of ESCA data is difficult and normally requires comparison to standards in a similar matrix. Also assumptions about depth profile and homogeneity of the sample can affect the ultimate accuracy of the quantification. One approach (Novakov) was to scan the sample with XRF to quantify the Pb present in the sample and then measure the S to Pb for each oxidation state of sulfur with ESCA. The S/Pb ratio multiplied by the Pb content in µg/m³ allowed calculations for atmospheric concentrations of S compounds.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE ESCA can be used on any gases, liquids and solids, depending on the accessory equipment available for the ESCA system. Elements from Li to V can be studied. B) INTERFERENCES/LIMITATIONS As in any direct compound identification, the equipment is costly (\$100 K), complicated and not readily available. Samples must be sent to commercial laboratories specializing in ESCA analysis. This instrument is extremely useful for qualitative work, but further work is needed on methods to quantify the results. C) RECOMMENDED USE AREA Valence state analysis of solid samples.		
5. OPERATIONAL PARAMETERS		
A) RANGE Elements from Li to V, sensitivity 10⁻² to 10⁻³ atomic fraction. B) ACCURACY N/Q C) PRECISION N/Q		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
N/A		ESCA System - Commercial suppliers: Hewlett-Packard Corp., Palo Alto, Ca.; McPherson Instr., Acton, Mass.; E.I. duPont, Monrovia, Ca.
8. KEYWORD INDEX: Analysis, compound identification, ESCA.		
9. CROSS REFERENCE ID NUMBERS 02-01-02.		
10. REFERENCES		
A) PRIMARY SOURCE 388 Siegbahn, K., et al, "Electron Spectroscopy for Chemical Analysis," <i>Nova Acta Regiae Soc. Sci. Upsaliensis</i>, Ser. IV, Vol. 20 (1967), NTIS No. AD 841-315. B) BACKGROUND INFORMATION 389 Evans, C.A., "Surface & Thin Film Compositional Analysis: Description & Comparison of Techniques," <i>Anal. Chem.</i>, 47, 819A (1975). 390 Evans, C.A., "Surface & Thin Film Analysis: Instrumentation," <i>Anal. Chem.</i>, 47, 855A (1975). C) FIELD APPLICATIONS 391 Novakov, T., A. Alcocer, P. Mueller and J. Ottovs, "Chemical Composition of Pasadena Aerosol by Particle Size and Time of Day," <i>J. Coll. Interface Sci.</i>, 39(7), 225 (1972). 392 Hulett, L.D., "Studies of Sulfur Compounds Adsorbed on Smoke Particles and Other Solids by Photoelectron Spectroscopy," <i>Proceedings of the Symposium on Air Quality</i>, 161st National Meeting of ACS, April 1-2, 1971, Los Angeles, California (Plenum Publishing, Washington, D. C.). 393 Craig, N.L., "Determination of the Chemical Status of Sulfur in Ambient Pollution Aerosols by X-Ray Photoelectron Spectroscopy," <i>Atm. Environ.</i>, 8, 15 (1974).		

1. TITLE CHEMICAL (ELEMENTAL) ANALYSIS USING SCANNING ELECTRON MICROSCOPE (SEM), ELECTRON PROBE MICROANALYSIS (EPMA) WITH AN ENERGY DISPERSIVE X-RAY SPECTROMETER (EDX)	2. IDENTIFICATION CODE 02-04-02-03
3. ABSTRACT OF METHODOLOGY Energy dispersive X-ray spectrometry (EDX) has replaced the more conventional wavelength dispersive spectrometry (WDS) in most SEM (02-04-01-04) and EPMA (02-04-01-03) systems. The WDS system uses a dispersive crystal through which the X-rays which are emitted from the sample are diffracted. The various X-ray wavelengths are dispersed to different angles. The X-ray spectrum is then obtained by plotting intensity versus diffraction angle. In the EDX techniques, however, the emitted X-rays are detected directly without the use of a crystal. The energy of the X-rays is measured by means of balance filters, selective excitation or pulse height analysis. The appropriate atomic numbers can then be assigned to the spectral peaks once their energies are determined. Elemental ratios are calculated and the compounds present are identified. EDX has several advantages: 1) it requires only a small X-ray source for sample excitation, 2) it provides direct observation, 3) the intensity of the signal is high, and 4) data acquisition time is short. However, WDS must be used to resolve elements from S to Ni.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE Method is applicable to the elemental analysis of particulates from flue, fugitive emissions, and solid samples.	
B) INTERFERENCES/LIMITATIONS Although relatively long counting times are required for elements present in trace amounts, EDX instrument stability limits counting time to 10 or 15 minutes, in practice. At high count rates, peaks may broaden. Particles in close proximity may interfere and preclude unambiguous analysis.	
C) RECOMMENDED USE AREA This method can be used to identify single particles through morphology and elemental analysis.	
5. OPERATIONAL PARAMETERS	
A) RANGE Elements present in less than 100 ppm concentrations can be identified, if background intensity is subtracted.	
B) ACCURACY 10% or less relative error.	
C) PRECISION Dependent upon peak resolution; values not quoted.	
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED
N/A	SEM or EPMA equipment with energy dispersive spectrometer.
8. KEYWORD INDEX: Energy dispersive spectrometry (EDX), Scanning electron microscopy (SEM), electron probe microanalysis (EPMA), particulates, quantitative analysis.	
9. CROSS REFERENCE ID NUMBERS 01-04-01-01, 01-04-02-01; 01-06-01-01, 01-06-02-01; 02-04-01-03; 02-04-01-04.	
10. REFERENCES	
A) PRIMARY SOURCE 362 Goldstein, J.I., and H. Yakowitz, "Practical Scanning Electron Microscopy," New York, Plenum Press, 1975, p. 402-3. 394 "Advances in X-ray Analysis," Vol. 15, (K.F.J. Heinrich, ed.), New York, Plenum Press, 1972, p. 197.	
B) BACKGROUND INFORMATION 395 DeHoff, R.T., and F.N. Rhines, "Quantitative Microscopy," New York, McGraw-Hill, 1968.	
C) FIELD APPLICATIONS 396 Ruff, A.W., Jr., "National Bureau of Standards Report, NBSIR," 74-474, 1974, p. 15. 397 Baynard, M., in "Microprobe Analysis," (C.A. Anderson, ed.), New York, Wiley, 1973, p. 323.	

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- 02-05-01-04 Continuous On-Line Gas Monitoring Systems Design
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02-05-02 On-Line Continuous Gas Analysis

- 02-05-02-01 Continuous Monitoring of NO/NO₂
- 02-05-02-02 Continuous Monitoring of Ozone
- 02-05-02-03 Continuous Monitoring of Sulfur Dioxide
- 02-05-02-04 Continuous Monitoring of CO/CO₂
- 02-05-02-05 Continuous Monitoring of H₂S
- 02-05-02-06 Determination of Hydrocarbons Corrected for Methane

02-05-03 On-Line Continuous Liquid Analysis

- 02-05-03-01 Continuous On-Line Liquid Analysis With a Technicon Monitor IV System
- 02-05-03-02 Continuous On-Line Monitoring of Liquid Streams With Orion Specific Ion Electrodes

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APPLICATION MATRIX FOR 02-05 ON-LINE CONTINUOUS ANALYSIS

METHOD	LEVEL I ENVIRONMENTAL ASSESSMENT	COMPLIANCE	ENGINEERING EVALUATION R/D
02-05-01-01			●
02-05-01-02			●
02-05-01-03	●		●
02-05-01-04			●
02-05-01-05			●
02-05-02-01	●		●
02-05-02-02	●	●	●
02-05-02-03	●	●	●
02-05-02-04	●	●	●
02-05-02-05	●		●
02-05-02-06		●	
02-05-03-01			●
02-05-03-02	●		●

ON-LINE CONTINUOUS ANALYSIS - ID No. 02-05

This section contains methods for continuous analysis of gases and liquids under flue gas, fugitive (ambient), or process stream conditions. The measurement methods discussed in this section are designed for continuous automated operation. While a compilation of methods has been given for each gas discussed, specific instruments have been recommended as the best choice for flue gas and fugitive monitoring.

02-05-01 On-Line Gas Analysis/Sampling (Abstracts 02-05-01-01 through 02-05-01-04)

Analysis of the gases by a specific instrumental technique is only part of the problem of on-line analysis. Sampling is an integral part of on-line continuous analysis, especially for gases. Section 02-05-01 contains specific procedures for gas sampling system design. Each particular source will have its own unique problems but, in general, the following concepts can be applied to all systems.

1. Sampling location and frequency - Sampling site and number of sampling points should be selected to obtain representative samples. Attention should be directed to local meteorological conditions, unintentioned proximity to sources, and possible anomalies in the parent air, especially when sampling for fugitive emissions (01-05). The cyclic nature of many processes should be considered in establishing the sampling times and lengths.

2. Gas flow characteristics - The sample should flow readily despite changes in temperature or pressure. Sample lines should be protected from clogging by particulates and/or condensation (02-05-01-01).

3. Removal of interferences - Converters or filters are employed to remove species that can affect the system accuracy or operation (02-05-01-01). These systems must be chosen with care to avoid removing or changing the species of interest.

4. Sample conditioning - The collection device or analyzer may require the sample to be within specified limits of temperature, pressure or humidity (02-05-01-02, -03). It is recommended that for SO_2 and CO_2 monitoring, the membrane system of gas conditioning be used (02-05-01-02).

5. Sampling train materials - Absorption, adsorption, condensation and other chemical reactions can occur in the sampling system. When temperature conditions allow, heat-traced Teflon tubing should be used (02-05-01-04). For higher temperatures, borosilicate glass or 316 stainless steel lines can be used.

6. Calibration - Whenever possible, dynamic calibration under simulated conditions is the desired approach. The concentrations of the calibration gases should test the dynamic range of the instrument (02-05-02-01, 02, 03, 04, 05). Recent studies (reference 170, 171) have shown that aluminum cylinders provide the best stability for storing certified gases.

02-05-02 On-Line Continuous Gas Analysis (Abstracts 02-05-02-01 through 02-05-02-05)

In abstracts 02-04-01-01 through 02-04-01-05, currently available commercial approaches to on-line continuous monitoring of carbon dioxide, carbon monoxide, ozone, NO_x , sulfur dioxide, and hydrogen sulfide are presented. The methods employed include colorimetric (NO_x , O_3 , H_2S) and coulometric (NO , O_3 , CO , H_2S) techniques, GC (CO_2 , H_2S), NDIR (NO , SO_2 , CO , CO_2), NDUV (NO_x , SO_2), Dispersive Spectroscopy (O_3 , CO , CO_2), electrochemical methods (NO_x , DO_2 , CO , H_2S), second derivative spectroscopy (NO , SO_2 , O_3), correlation spectroscopy (SO_2 , NO), chemiluminescence (NO , O_3 , SO_2), fluorescence (SO_2 , CO) and catalytic oxidation (CO). For each gas, the different methods are outlined and describe operating principles, the species measured, sensitivity, range, and interferences. It is also noted whether the particular instrument can be used to sample fugitive emissions, flue gas emissions, or both. For each gas a specific instrument is recommended for fugitive and flue gas monitoring.

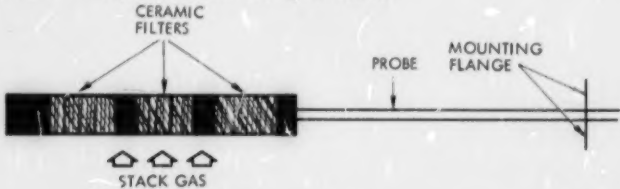
02-05-03 On-line Continuous Liquid Analysis (Abstracts 02-05-03-01 to 02-05-03-02)

On-line continuous liquid analysis is not as developed as on-line gas analysis. While many instruments are available for pH and temperature monitoring, there are far fewer instruments capable of monitoring specific anions or cations. Abstracts 02-05-03-01 and -02 discuss the procedures for using the Technicon and Orion continuous monitor systems. These systems take the colorimetric and specific ion electrode approaches, respectively.

While these systems require only small (ml) amounts of the process stream to pass through their flowthrough systems, the same problems that are involved with liquid/slurry (01-02) sampling must be considered. The reader is directed to 01-02 to review the problems involved in obtaining a representative liquid sample.

REFERENCES

- 171 Wechter, S.G., "Preparation of Stable Pollution Gas Standards Using Treated Aluminum Cylinders," ASTM Calibration Symposium, Boulder, Colorado, August 5, 1975.
- 170 Grieco, H.A., and S.G. Wechter, "The Trouble with Reactive Calibration-Gas Blends and What To Do About It," Gulf Coast Instrumental Analysis Conference, Houston, Texas, November 1, 1974.

1. TITLE PROBE AND FILTERS FOR ON-LINE MEASUREMENT OF FUGITIVE EMISSIONS OR FLUE GAS	2. IDENTIFICATION CODE 02-05-01-01
3. ABSTRACT OF METHODOLOGY	
In order to analyze a gas stream by continuous on-line instruments, a gas sample must be continuously extracted from the gas stream and the particulates removed. For fugitive emissions a Teflon line (probe) and Teflon or glass filter will suffice. In flue gas streams, a more elaborate system must be devised because of the higher temperatures and mass readings. The probe is kept at stack temperatures by the gas stream or by a heating jacket, but never below 110°C. The recommended materials are 316 SS or Inconel. Figure 02-05-01-01A shows a probe developed for high dust loadings. The large filter area allows long time intervals between changes. An equally usable approach is to install a filter plug of ceramic or stainless steel mesh and periodically backflush with line air to clean the filter. For high temperature applications (>500°C), water cooled probes are recommended. A typical high temperature probe consists of a water or steam jacket with a quartz liner. This probe has been used up to 1000°C.	
	
Figure 02-05-01-01A. (From Pol. Eng., 26 (July, 1975)).	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE The equipment described can be used in flue gas streams at temperatures up to 1000°C.	
B) INTERFERENCES/LIMITATIONS The particulate loading in the filter should be kept low to prevent gases adsorbing on particulates. Chemical reactions on the particulates might affect the concentration or composition of gas sampled.	
C) RECOMMENDED USE AREA Engineering evaluation R&D; proposed compliance method for aluminum refinery.	
5. OPERATIONAL PARAMETERS	
A) RANGE Up to 1000°C. B) ACCURACY N/A C) PRECISION N/A	
6. REAGENTS REQUIRED None	7. EQUIPMENT REQUIRED Teflon tubing, 316 SS tubing, quartz tubes, SS water jacket.
8. KEYWORD INDEX: Analysis, probes.	
9. CROSS REFERENCE ID NUMBERS 02-05-02.	
10. REFERENCES	
A) PRIMARY SOURCE 398 Wolf, P.C., "Continuous Stack Gas Monitoring: Gas Handling Components and Accessories," Pol. Eng., 26 (July 1975).	
B) BACKGROUND INFORMATION 018 Flegal, C.A., M.L. Kraft, C. Lin, R.F. Maddalone, J.A. Starkovich and C. Zee, "Procedures for Process Measurements: Trace Inorganic Materials," TRW Systems Group, EPA Contract #68-02-1393, July 1975.	
C) FIELD APPLICATIONS	

1. TITLE MEMBRANE CONDITIONING SYSTEM FOR ON-LINE CONTINUOUS MONITORING OF ATMOSPHERIC AND FLUE GASES	2. IDENTIFICATION CODE 02-05-01-02
3. ABSTRACT OF METHODOLOGY	
Many of the atmospheric or flue gas instrumental measurement methods require that the gas stream be conditioned prior to the actual analysis of the gas. The particulates are first removed (see 02-05-01-01) and then the moisture content of the stream is reduced. At all times, the gases are conveyed in either SS or Teflon heat traced lines to prevent condensation prior to the gas conditioning. Figure 02-05-01-01A is a drawing of the membrane system for moisture separation. This unit operates by passing the wet sample flow into the sample inlet which wets the inside wall of the tube. Water in the sample is continuously removed as water vapor on the shell side at the purge outlet, by dry gas flowing counter-current to the sample flow. This type of system is highly recommended for the analysis of gases which have a high solubility in water (carbon dioxide, sulfur dioxide) and thus could be entrained in the condensate of a refrigeration type unit. The upper temperature range of the unit is approximately 150°C.	
4. APPLICATION: Engineering evaluation R&D.	
A) OPERATIONAL SCOPE The sample conditioning methods in this abstract can be used for atmospheric or flue gas monitoring. B) INTERFERENCES/LIMITATIONS This gas conditioning system is only useful to 150°C. For higher temperature applications, use 02-05-01-03. C) RECOMMENDED USE AREA This unit is recommended for all levels to remove moisture from flue gas streams, especially when SO₂ or CO₂ is to be measured.	
5. OPERATIONAL PARAMETERS	
A) RANGE Up to 150°C. B) ACCURACY NA C) PRECISION NA	
6. REAGENTS REQUIRED None	7. EQUIPMENT REQUIRED Membrane dryer (Perma Pure Products, Oceanport, N.J., is a possible source).
8. KEYWORD INDEX: Analysis, sample conditioning.	
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02-05-01-03, 02-05-01-04.	
10. REFERENCES	
A) PRIMARY SOURCE 390 Perma Pure Products, Oceanport, N.J., Engineering Brochure. B) BACKGROUND INFORMATION 391 Chapman, R.L., <u>Pol. Eng.</u>, 4(6), 38 (1972). 392 Lierop, B.V., Preprint, presented at 24th National Plant Engineering and Maintenance Conference, Chicago, Ill., March 9, 1973. 393 Morrow, N.L., R.R. Bertrand and R.S. Brief, <u>Chem. Eng.</u>, 79(2), 84 (1972). C) FIELD APPLICATIONS	

TITLE MEMBRANE CONDITIONING SYSTEM FOR ON-LINE CONTINUOUS MONITORING OF
ATMOSPHERIC AND FLUE GASES (CONTINUED)

ID NO. 02-05-01-02

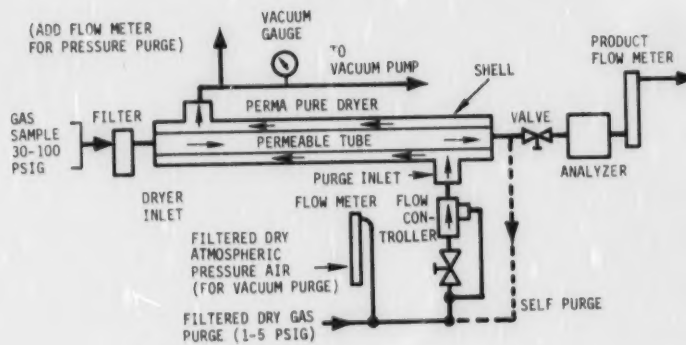


Figure 02-05-01-02A. (From Reference 390).

1. TITLE GAS CONDITIONING BY CONTROLLED CONDENSATION		2. IDENTIFICATION CODE 02-05-01-03
3. ABSTRACT OF METHODOLOGY		
Flue gases can be cooled to lower the moisture content of the gas stream. Figure 02-05-01-03A shows a typical design for a condenser system. An electromechanical refrigerator is the most satisfactory device for condensate separation, but conditions (limited electrical power) or complexity can dictate the use of ice/water or dry ice cooling. The condensing section is designed so that the sample gas will have short residence times in the cooling coil. Also, the cooling coil-condensate collector is such that the gas does not flow over the collected condensate surface. Both of these conditions will minimize the amount of gas (especially CO₂ and SO₂) that will go into solution.		
4. APPLICATION: Environmental assessment, engineering evaluation R&D.		
A) OPERATIONAL SCOPE Moisture removal in flue gas streams is particularly important. This condensation method of moisture removal can be used in all areas, but it is primarily intended to be used in high temperature (>150°C) and survey (level I environmental assessment) work. Depending on material design (Pyrex, quartz or stainless steel) the temperature range of the condenser system is limited only by its ability to cool the gas stream to a constant temperature. B) INTERFERENCES/LIMITATIONS Whenever a condenser system is used to remove excess moisture from a gas stream, it is possible that gas concentrations could be changed by the scrubbing action of the condensation mechanism (SO₂ and CO₂) or that a chemical change in the gas composition can be induced (SO₂ $\xrightarrow{H_2O}$ H₂SO₄). Precautions as noted in Abstract of Methodology must be followed to limit these two possibilities. C) RECOMMENDED USE AREA Environmental assessment.		
5. OPERATIONAL PARAMETERS		
A) RANGE Up to 1000°C. B) ACCURACY N/Q ($\pm 10\%$ of actual gas concentrations estimated). C) PRECISION N/Q ($\pm 10\%$ estimated).		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Ice/water or antifreeze recirculating fluid.		Commercial condenser unit (Beckman Instr., Fullerton, Ca.; Joy Manufacturing Co., Los Angeles, Ca.) or constructed as shown in Figure 02-05-01-03A.
8. KEYWORD INDEX: Analysis, gas conditioning, moisture condensation.		
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02-05-01-02.		
10. REFERENCES		
A) PRIMARY SOURCE 398 Wolf, P.C., "Continuous Stack Gas Monitoring: Gas Handling Components and Accessories," <i>Pol. Eng.</i>, 26 (July 1975). B) BACKGROUND INFORMATION C) FIELD APPLICATIONS		

TITLE GAS CONDITIONING BY CONTROLLED CONDENSATION (CONTINUED)

ID NO. 02-05-01-03

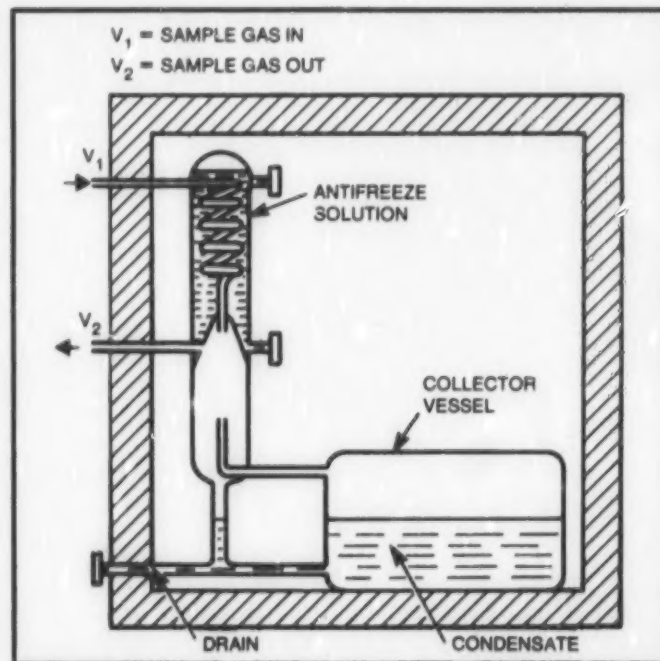


Figure 02-05-01-03A. Schematic of Condenser Coil (from Reference 398).

1. TITLE CONTINUOUS ON-LINE GAS MONITORING SYSTEMS DESIGN	2. IDENTIFICATION CODE 02-05-01-04
3. ABSTRACT OF METHODOLOGY The ultimate performance of an analyzer will depend on how the sampling system (probe, lines, conditioning equipment, analyzer and pumps) is designed. In all system designs, the calibration gas must be conditioned in the same fashion as the sample gas. These calibration gases should be stored in aluminum-lined bottles (AIRCO) which have demonstrated improved reliability over conventional steel containers. In general, the distance between the analyzer and the sampling point should be minimized. If this is not possible, a bypass system is employed using high flow rate for gas sampling and line purge while a small quantity is drawn off for analysis. In all cases, heat traced ($\sim 125^{\circ}\text{C}$) stainless steel or Teflon lines are to be used to conduct the gas to the analyzer. Figure 02-05-01-04A shows a simple approach to single gas analysis system; Figure 02-05-01-04B shows a semi-automated multigas sampling system specifically designed to use a membrane gas conditioning unit. Figure 02-05-01-04C shows the schematic of a double pass fast-responding bypass system designed to monitor SO_2 inlet and outlet to FGD unit. This design assures that H_2SO_4 and H_2SO_3 aerosols will not precipitate in the sample lines.	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE These systems are designed to operate at high or low mass loadings and up to temperatures of 1000°C (when refrigeration is used to condition the gas). Membrane conditioning equipment requires that the gas be cooled to temperatures less than 150°C. See 02-05-01-01, 02, 03 for information about individual components. B) INTERFERENCES/LIMITATIONS The system must be adjusted to individual situations and problems such as high mass loading, corrosive gases and gases measured. These factors all affect the ultimate reliability of the gas sampling system. C) RECOMMENDED USE AREA Engineering evaluation R&D for flue gas sampling.	
5. OPERATIONAL PARAMETERS A) RANGE Up to 1000°C. B) ACCURACY N/Q ($\pm 10\%$ estimated). C) PRECISION N/Q ($\pm 10\%$ estimated).	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED See Figures 02-05-01-04A through C for equipment needs.
8. KEYWORD INDEX: Analysis, gas analysis, system design.	
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02, 03.	
10. REFERENCES A) PRIMARY SOURCE 399 Wolf, P.C., "Continuous Stack Gas Monitoring: Systems Design," <u>Pol. Eng.</u>, 36 (Aug. 1975). B) BACKGROUND INFORMATION 053 ASTM, "Tentative Recommended Practice for General Ambient Air Analyzer Procedures," 1974 Annual Book of ASTM Standards, Part 26, D3249-73T, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 708. 053 ASTM, "Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors," 1974 Annual Book of ASTM Standards, Part 26, D16-05-60, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 285. 053 ASTM, "Standard Recommended Practice for Planning the Sampling of the Atmosphere," 1974 Annual Book of ASTM Standards, Part 26, E1357-57, American Society for Testing and Materials, Philadelphia, PA., 1971, p. 271. C) FIELD APPLICATIONS	

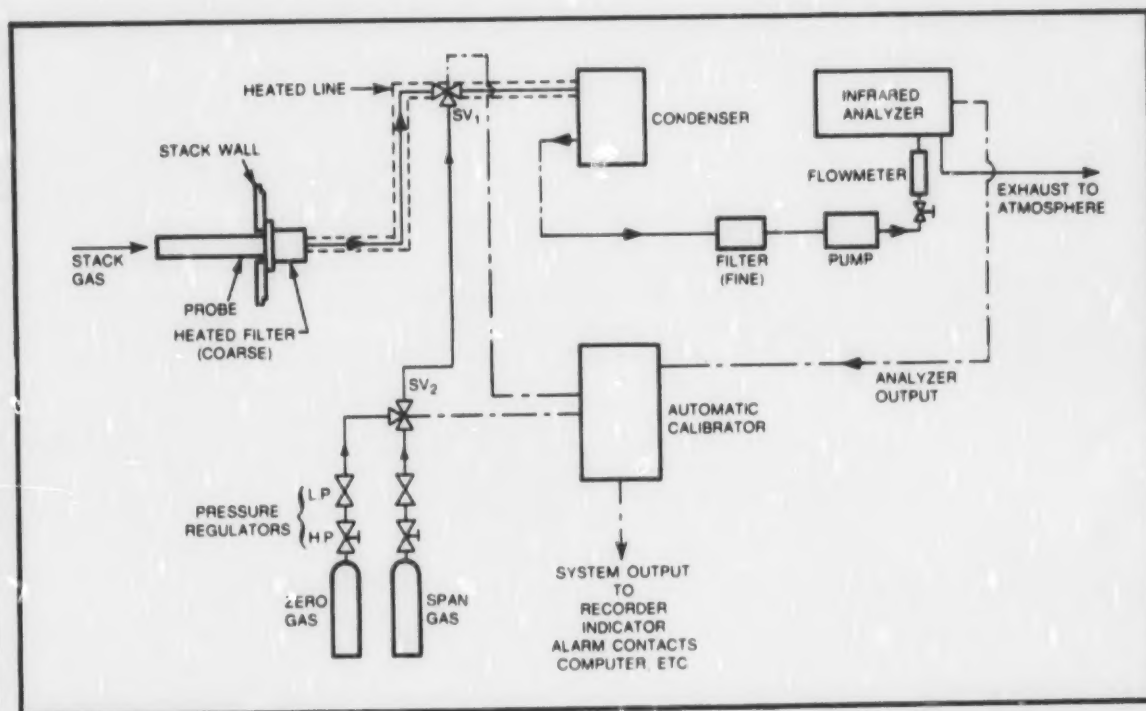
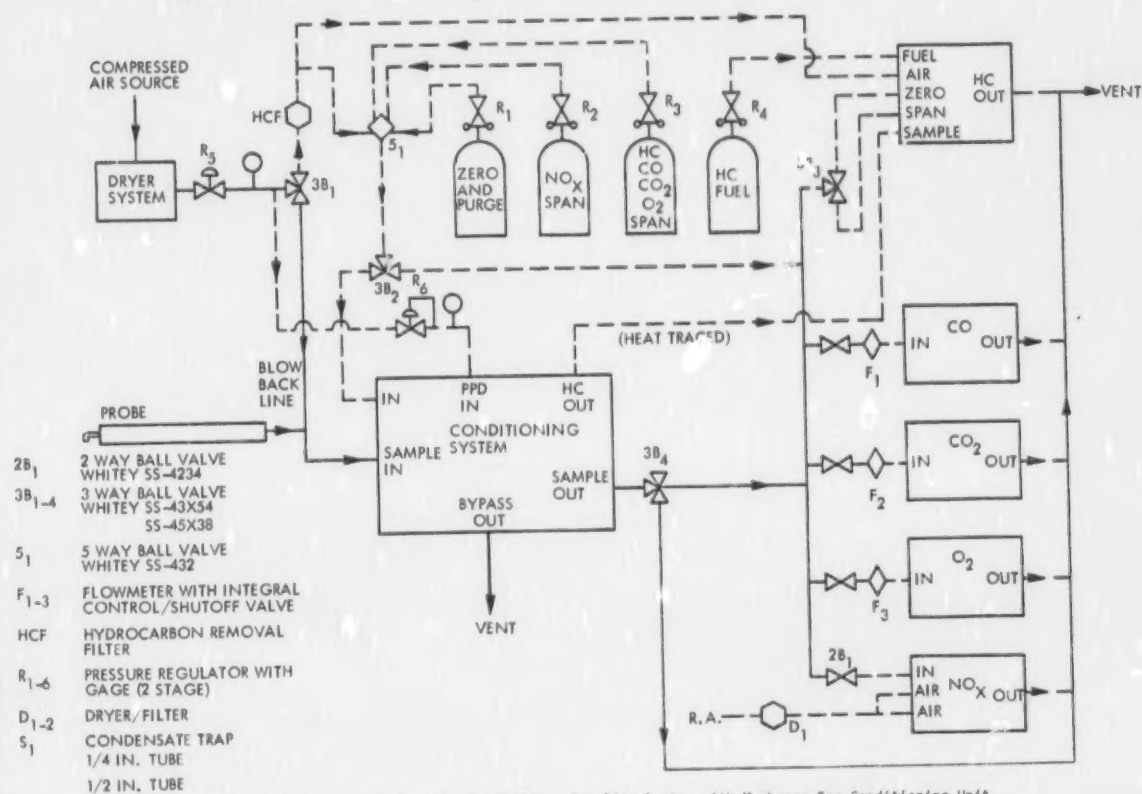
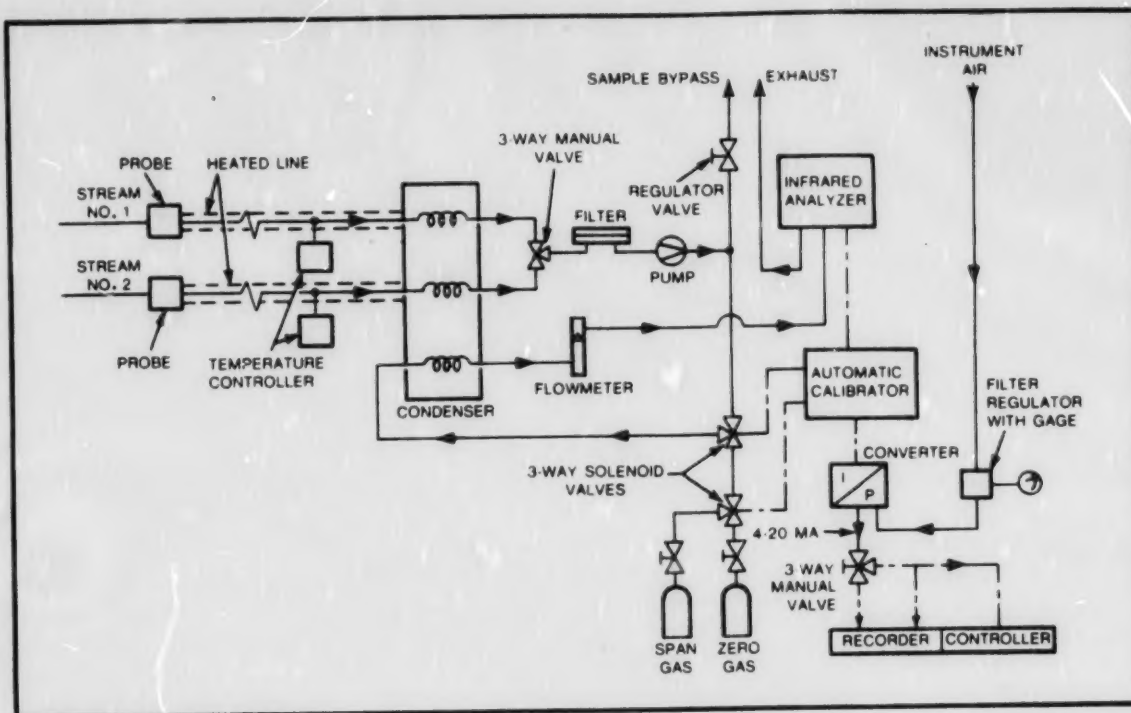
Figure 02-05-01-04A. Schematic of SO₂ Monitoring System With Second Passthrough Condenser (Reference 39B).

Figure 02-05-01-04B. Semi-automatic Multigas Sampling System with Membrane Gas Conditioning Unit.

Figure 02-05-01-04C. Schematic of Automatic SO₂ Monitoring System (Reference 399).

1. TITLE MULTIPORT PROBE FOR CONTINUOUS GAS MONITORING	2. IDENTIFICATION CODE 02-05-01-05
3. ABSTRACT OF METHODOLOGY Because of gas stratification in flue gas ducts, it is recommended that a multiport probe be designed and built for continuous gas sampling in a duct. The fabric design considerations are quite simple: 1) the probe should draw samples at a number of evenly spaced points along a line across the duct, 2) the same sample rate should be maintained at each sampling point, and 3) the samples from each point should be mixed and drawn through a single sampling line. Figure 02-05-01-05A is a schematic of the basic multiport design. Eight holes are drilled at evenly spaced distances along the sampling tube. For a 0.5 lpm flowrate, a 1.295 mm hole (or approximately a #55 drill) is drilled (see primary source for calculations at other flowrates). The tube should also be equipped with backflushing capability to periodically purge the holes of particulates. An internal filter should also be used to prevent fine particles from reaching the sample lines (see 02-05-01-01).	
4. APPLICATION: Engineering evaluation R&D. A) OPERATIONAL SCOPE This probe is designed to obtain representative gas samples under stratified gas conditions. The probe is designed to operate under moderate grain loading at temperatures and conditions acceptable to 316 SS or Inconel. B) INTERFERENCES/LIMITATIONS Particulates can enter probe, so an internal filter is required. Ports must face into the flow. (See primary source for advanced design considerations.) C) RECOMMENDED USE AREA This is the recommended probe for continuous gas analysis by on-line instrumentation for all levels.	
5. OPERATIONAL PARAMETERS A) RANGE Moderate grain loading and temperatures and conditions suitable to 316 SS or Inconel. B) ACCURACY $\pm 6\%$ C) PRECISION $\pm 5\%$	
6. REAGENTS REQUIRED N/A	7. EQUIPMENT REQUIRED See Figure 02-05-01-05A.
8. KEYWORD INDEX: Sampling, gases, multiport sampling probe.	
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02, 03, 04.	
10. REFERENCES A) PRIMARY SOURCE 400 Brooks, E.F., C.A. Flegal, L.N. Harnett, M.A. Kolpin, D.J. Luciani and R.L. Williams, "Continuous Measurement of Gas Composition from Stationary Sources," EPA-600/2-75-012, TRW Defense and Space Systems, Redondo Beach, Ca., July 1975. B) BACKGROUND INFORMATION 401 Zakak, et al, "Procedures for Measurement in Stratified Gases," EPA-650/2-74-086-a and -b, September 1974. C) FIELD APPLICATIONS	

TITLE MULTI-PORT PROBE FOR CONTINUOUS GAS MONITORING (CONTINUED)

ID NO. 02-05-01-05

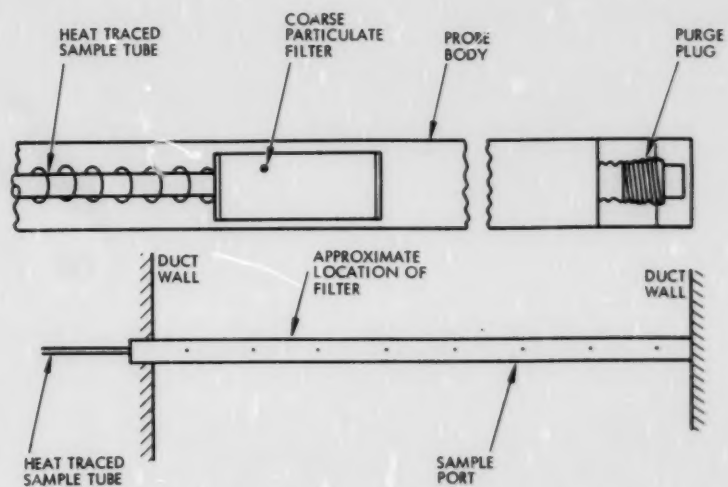


Figure 02-05-01-05A. Multi-hole Sampling Probe.

2. IDENTIFICATION CODE

02-05-02-01

1. TITLE CONTINUOUS MONITORING OF NO/NO₂

3. ABSTRACT OF METHODOLOGY

Table 02-05-02-01A summarizes representative equipment for NO/NO_x analysis. The recommended method for fugitive emissions is either chemiluminescent NO/NO_x or coulometric analyzer. The chemiluminescent approach is favored for its higher sensitivity and specificity. For flue gas analysis the NDIR unit or the chemiluminescent unit are recommended. The NDIR unit is favored for continuous process monitoring, while chemiluminescent unit is better for engineering evaluation or level 2 environmental assessment. While no instrument is recommended for remote sensing, the Barringer Cospec unit has proven its utility in the field.

4. APPLICATION: Engineering Evaluation R&D, Environmental Assessment.

A) OPERATIONAL SCOPE

See Table 02-05-02-01A.

B) INTERFERENCES/LIMITATIONS

See Table 02-05-02-01A.

C) RECOMMENDED USE AREA

See Abstract of Methodology.

5. OPERATIONAL PARAMETERS

A) RANGE See Table 01-05-02-01A.

B) ACCURACY See Table 01-05-02-01A.

C) PRECISION See Table 01-05-02-01A.

6. REAGENTS REQUIRED

Calibration gases.

7. EQUIPMENT REQUIRED

See Table 01-05-02-01A.

8. KEYWORD INDEX: Analysis, continuous monitoring, NO₂, NO.

9. CROSS REFERENCE ID NUMBERS 01-05-01-01, 02, 03, 04.

10. REFERENCES See Table 01-05-02-01A.

A) PRIMARY SOURCE

B) BACKGROUND INFORMATION

C) FIELD APPLICATIONS

TITLE CONTINUOUS MONITORING OF NO/NO₂ (CONTINUED)

ID NO. 02-05-02-01

Table 02-05-02-01A. Representative Instruments for On-Line Continuous Monitoring of NO/NO_x.

Representative Manufacturer/Model	Principle of Operation	Species Monitored	Range	Sensitivity	Fugitive Emissions	Flue Gas Emissions	Interferences/Remarks	Ref.
Barringer Cospec IV	Correlation Spectroscopy. Instrument consists of 2 telescopes, a 2-grating spectrometer for dispersion, a disc shaped multiple slit mask, and electronics. Disc mask is a high contrast ref. spectrum for correlation against incoming absorption spectra. Photomultiplier tubes detect light modulations produced by rotation of the disc. Unit continuously measures optical depth in ppm-meters of gas cloud under observation and uses sky light as source of radiation.	NO ₂	1-700 ppm meters	1 ppm-meter	Yes	Yes*	*Normal source analysis consists of monitoring stack plume. Monitors NO ₂ .	402, 403
Beckman Model 909	Coulometric. Inlet gas passes thru selective scrubber to remove SO ₂ , O ₂ , NO ₂ , mercaptans and H ₂ S from sample. The NO is reacted with ozone and the NO ₂ formed reacts with I ₃ in electrolyte producing I ₂ . The I ₂ is reduced at the cathode and the current required is proportional to the NO.	NO	0-1.0 ppm (3 ranges)	4 to 100 ppb (depending on range)	Yes	No	O ₃ , SO ₂ , H ₂ S, NO ₂ and RS must be removed prior to analysis.	405, 411
Model 910	Coulometric. Selective scrubber removes O ₃ , SO ₂ , H ₂ S from sample. The NO ₂ reacts with I ⁻ in electrolyte producing I ₂ . The I ₂ is reduced at the cathode and the current required is proportional to the NO ₂ .	NO ₂	0-1.0 ppm (3 ranges)	4 to 100 ppb (depending on range)	Yes	No	O ₃ , SO ₂ , H ₂ S and RS must be removed prior to analysis.	405, 414, 411
Beckman Model 865	NDIR. Differential absorption of infrared energy measured by a selective gas microphase detector in a dual beam optical system.	NO	0-100% (0-500 ppm)	0.5% full scale	No	Yes	Can operate in relative humidities up to 100%.	405, 406
DuPont Model 461	NDUV. A beam of light is passed thru the sample, then split and monitored.	NO _x	0-100 ppm 0-100%	5 ppm	No	Yes	Water interference <2.8% of NO _x signal. SO ₂ interference <0.45% of NO _x signal.	406
Dynasience P100D	Electrochemical cell. Instrument includes sampling and conditioning equip. to monitor source gases. Sample acquired thru use of heated sintered SS filter and heated sample lines. Principle of operation is based on the combined use of a semi-permeable membrane and liquid state controlled oxidation-reduction.	NO _x /NO ₂	0-2000 (3 ranges)	2% of full scale	No	Yes	Interferences removed via internal sample conditioning.	407, 408
Lear Siegler Spectrometrics I	Second Derivation Spectroscopy and Ultraviolet region from 190 nm-400 nm is automatically scanned and a second derivative spectra is produced whose peak location and intensity identifies the pollutant and its concentration.	NO/NO ₂	0-10 ppm (4 ranges)	0.006 ppm NO 0.040 ppm NO ₂	Yes	No	Interferences must be detected thru manual scan.	409, 410
Technicon Air Monitor IV	Colorimetric. NO ₂ is monitored directly using a modified Saltzman reaction (diazotization and coupling). NO _x is found by oxidizing NO with chromium trioxide and subsequent measurement of NO ₂ using a modified Saltzman method.	NO ₂ /NO _x	0-0.15 ppm	0.0015 ppm	Yes	No	A 5x ozone concentration to NO ₂ will cause slight interference. A 30x sulfur dioxide conc. to NO ₂ might bleach the pink azo dye to a slight extent.	404, 405
Therm Electron	Chemiluminescent. NO and O ₃ react (NO+O ₃ →NO ₂ +O ₂ +hv) and emit light at 0.6-3μ. A high sensitivity photomultiplier monitors the light emitted in the reaction chamber. NO _x is determined in the same fashion after NO ₂ is reduced to NO in a catalytic converter.	NO/NO _x	0-2500 ppm (9 ranges)	1 ppb	Yes	Yes	Interferences commonly found in ambient air amount to <0.5 on most sensitive range (0-0.01 ppm).	405, 412, 413

TITLE CONTINUOUS MONITORING OF NO/NO₂ (CONTINUED)

ID NO. 02-05-02-01

Table 02-05-02-01A (Continued)

- 402 Newcomb, T.S., and M.M. Millan, IEEE Trans. Geo. Elect., GE-8, 149 (1970).
- 403 McCreight, C.R., and C.L. Tien, "Interpretation Problems in the Correlation Map Sensing Techniques," presented at the Joint Conference on Sensing of Environmental Pollutants, Palo Alto, Calif. (Nov. 8-10, 1971); Available from AIAA Library, 750 Third Avenue, New York, N.Y.
- 404 Harman, J.N., "Continuous Colorimetric Analysis of Ambient Oxides of Nitrogen (NO and NO₂)," Adv. Instr., 26, Part 1, Oct. 1971.
- 405 Decker, C.E., T. Royal and J. Tommerdahl, "Field Evaluation of New Air Pollution Monitoring Systems," Final Report of Research Triangle Institute, Research Triangle Park, N.C., EPA Contract #CPA70-101, May 1972.
- 406 Saltzman, R.S., and J.A. Williamson, "Monitoring Stationary Source Emissions for Air Pollutants with Photometric Analyzer Systems," Air Quality Instrumentation, Vol. 1, Instrument Society of America, Pittsburgh, Pennsylvania.
- 407 Shen, T.T., and W.N. Stasiuk, "Performance Characteristics of Stack Testing Instruments for Oxides of Nitrogen," APCA paper number 73-116, Presented at the 66th Annual Meeting of the Air Pollution Control Association, Chicago, Ill., June 1973.
- 408 Snyder, A.D., E. Eimutis, M. Konicek, L. Parts and P. Sherman, "Instrumentation for the Determination of Nitrogen Oxides Content of Stationary Source Emissions," Vol. 2, Report of Monsanto Research Corp., Dayton, Ohio, EPA Contract #EHS071-30, EPA Publication APTD-0942, Jan. 1972.
- 409 Hager, R.N., and R.C. Anderson, J. Opt. Soc. Amer., 60, 1444 (1970).
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- 411 Stevens, R.K., et al, "Field Performance of Advanced Monitors for All Sorts of Nitrogen, Ozone, Sulfur Dioxide, Carbon Monoxide, Methane, and Non-Methane Hydrocarbons," APCA Paper #72-13, Presented at the 65th Annual Meeting of the Air Pollution Control Assoc., Miami, Florida (June 18-22, 1972).
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1. TITLE CONTINUOUS MONITORING OF OZONE		2. IDENTIFICATION CODE 02-05-02-02	
3. ABSTRACT OF METHODOLOGY			
Table 02-05-02-02A summarizes representative equipment for continuous monitoring of O_3. The measurement of ozone is primarily devoted to fugitive emissions. The recommended unit for fugitive emissions is a chemiluminescent detector. If total oxidant is to be measured or greater sensitivity is required, an amperometric total oxidant unit can be used. The Moly instrument has been selected by the EPA as a reference method for ambient ozone measurements.			
4. APPLICATION: All areas.			
A) OPERATIONAL SCOPE These instruments are designed to operate in ambient conditions, but can be applied to flue gas monitoring. B) INTERFERENCES/LIMITATIONS The chemiluminescent detector is specific for ozone, while the amperometric detector responds to all oxidants. C) RECOMMENDED USE AREA The instruments discussed in the Abstract of Methodology can be used for all areas for fugitive emissions.			
5. OPERATIONAL PARAMETERS See Table 02-05-02-02A.			
A) RANGE B) ACCURACY C) PRECISION			
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED	
Calibration gases.		See Table 02-05-02-02A.	
8. KEYWORD INDEX: Analysis, continuous monitoring, NO , NO_2 .			
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02, 03, 04.			
10. REFERENCES See Table 02-05-02-02B.			
A) PRIMARY SOURCE B) BACKGROUND INFORMATION C) FIELD APPLICATIONS			

TITLE CONTINUOUS MONITORING OF OZONE (CONTINUED)					ID NO. 02-05-02-02			
Table 02-05-02-02A. Representative Continuous On-Line O ₃ Monitors.								
Representative Manufacturer/Model	Principle of Operation	Species Monitored	Range	Sensitivity	Fugitive Emissions	Flue Gas Emissions	Interferences/Remarks	Ref.
Beckman Model 90B	Amperometric. An air sample is drawn through a detector cell containing buffered KI. Oxidant in the air sample oxidizes the iodide to iodine which is sensed by the electrode system. The iodine produced is reduced at the cathode yielding a current proportional to the oxidant present in the air sample.	Total Oxidant	0-1 ppm (3 ranges)	4 ppb	Yes	No	This type of instrument does not monitor ozone concentration directly. Instead the total oxidant level is found.	405,414, 411,423, 424,423, 428,430, 436,438
Dasibi Model 1003-AH	Ultraviolet Absorption. The UV absorbance of reference gas stream (O ₃ reduced catalytically) and a sample stream are taken at 253.7 nm. The absorbance of the sample stream minus the reference absorbance is displayed on the instrument as ppm O ₃ .	O ₃	0.003-20 ppm	3 ppb	Yes	Yes	No interference from 1.0 ppm NO ₂ .	405,415, 416,431, 432,433
Lear Siegler Model III d ²	Second derivative Spectroscopy. Ultraviolet region at 263 μ is automatically scanned and a second derivative spectra is produced whose peak location and intensity identifies the pollutant and its concentration.	O ₃	0-10 ppm (4 ranges)	0.025 ppm	Yes	No	Interferences noted by manually scanning region of interest.	417,418, 434,435
Technicon Air Monitor IV	Colorimetric. Neutral KI is reduced by O ₃ releasing I ₂ . The quantity of I ₂ produced is monitored spectrophotometrically at 352 nm.	Total Oxidant	0-0.2 ppm	0.0015 ppm	Yes	Yes	Since this instrument is not specific to O ₃ , one must be aware that other oxidants in the air will also be measured. Nitrogen dioxide at 0.100 ppm will be read as 0.009 ppm O ₃ . A negative error from SO ₂ is reduced by using an oxidizing column to remove the SO ₂ .	405,414, 425,426, 430
Thermo Electron Model 10A	Chemiluminescence. NO ₃ + O ₃ → NO ₂ + O ₂ + hv (0.6-3 μ). In practice an unknown stream of O ₃ is combined in the reaction chamber with NO and the reaction is monitored with a photomultiplier.	O ₃	0-10,000 ppm (8 ranges)	0.1 ppm	Yes	Yes	No known interferences. This instrument can also measure NO by reversing the roles of the gases.	419,420, 421,422, 423,437, 439
Meloy Model OA 350-2R	Chemiluminescence. NO ₃ + O ₃ → NO ₂ + O ₂ + hv (0.6-3 μ). In practice an unknown stream of O ₃ is combined in the reaction chamber with NO and the reaction is monitored with a photomultiplier.	O ₃	0-0.5 ppm	0.1 ppm	Yes	No	No known interferences. This instrument can also measure NO by reversing the roles of the gases.	564

TITLE CONTINUOUS MONITORING OF OZONE (CONTINUED)

ID NO. 02-05-02-02

Table 02-05-02-02B

References for Ozone Continuous Monitors

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1. TITLE CONTINUOUS MONITORING OF SULFUR DIOXIDE		2. IDENTIFICATION CODE 02-05-02-03	
3. ABSTRACT OF METHODOLOGY			
Table 02-05-02-03A summarizes the representative equipment for SO₂ continuous monitoring. The recommended method for fugitive emission monitoring is the pulsed fluorescent instrument because of its sensitivity and specificity. For flue gas monitoring, either the NDIR or electrochemical instrument is recommended. The NDIR unit is more useful for continuous process monitoring, while the electrochemical unit's portability makes it more useful for environmental assessment. The Meloy (SA-185-2A) and the Thermo Electron units are designated as equivalent compliance methods for ambient measurements.			
4. APPLICATION: All areas.			
A) OPERATIONAL SCOPE The equipment listed in Table 02-05-02-03A can be used for fugitive emission or flue gas monitoring. B) INTERFERENCES/LIMITATIONS See Table 02-05-02-03A. C) RECOMMENDED USE AREA See Abstract of Methodology.			
5. OPERATIONAL PARAMETERS See Table 02-05-02-03A.			
A) RANGE B) ACCURACY C) PRECISION			
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED	
Calibration gases.		See Table 02-05-02-03A.	
8. KEYWORD INDEX: Analysis, continuous monitoring, SO ₂ .			
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02-05-01-02, 02-05-01-03, 02-05-01-04.			
10. REFERENCES See Table 02-05-02-03B.			
A) PRIMARY SOURCE B) BACKGROUND INFORMATION C) FIELD APPLICATIONS			

TITLE CONTINUOUS MONITORING OF SULFUR DIOXIDE (CONTINUED)					ID NO. 02-05-02-03			
Table 02-05-02-03A, Continuous Monitoring Methods for Sulfur Dioxide.								
Representative Manufacturer/Model	Principle of Operation	Species Monitored	Range	Sensitivity	Ambient Analysis	Source Analysis	Interferences/Remarks	References
MELOY Laboratory Model 185-2A Model FSA 190	Flame Photometric: Hydrogen rich flame chemiluminescent reaction. Photomultiplier pickup of emitted light.	Sulfur compounds	0.01 to 10 ppm 25 to 10,000 ppm	0.01 ppm 75 ppm	Yes No	No Yes	(Must be aware that all sulfur compounds are registered. Optional scrubbers available to remove interferences.	405,411, 443,444, 446,451, 565
Tracor 270HA	GC separation and then analysis by F.P. Detector.	SO ₂ , H ₂ S	0 to 100 ppb 0 to 1 ppm	1 ppb	Yes	No	Because of the GC, this instrument is specific for SO ₂ .	446, 451
Thermo Electron Corporation Model 43	Pulsed Fluorescent: Excitation of SO ₂ molecules by UV source. Fluorescence measured.	SO ₂	0 to 0.5 ppm 0 to 1 ppm 0 to 50 ppm (0 to 5000 ppm)	5 ppb	Yes	Yes	Instrument is specific for SO ₂ .	445, 566
Theta Sensors, Inc. Series 7100	Electrochemical: Chemical reaction occurs between a gas and a charged electrode to produce a current flow.	SO ₂	0 to 5000 ppm	0.01 ppm	Yes	Yes	Some sample conditioning registered for source monitoring. Full-scale concentration set with calibration gas.	447
Phillips Electronics PW 9700	Coulometric: Based on coulometric titration of SO ₂ with internal regenerated bromine	SO ₂	0 to 3 ppm	4 ppb	Yes	No	Specificity increased due to pre-filters to remove H ₂ S, ozone, etc.	435,440, 441,443
Lear Siegler SM 1000	Second derivative spectroscopy: Second derivative spectra generated whose intensity is proportional to the gas concentration.	SO ₂	0 to 0.5 ppm 0 to 2.0 ppm	0.010 ppm	Yes	No	Second derivative spectroscopy eliminates most wavelength interferences.	448
Wilks MIRAN-11	IR Spectroscopy: Narrow band pass filters used to remove all but analytical wavelength in IR region.	SO ₂	0 to 1% (variable)	0.14 ppm	Yes	Yes	Source analysis can be complicated by presence of water vapor.	449
Beckman Model 864 S	Nondispersive IR: Differential absorption of IR energy measured by a selective gas microphone detector in a dual beam optical system.	SO ₂	0 to 100%	0.5% full scale	Yes	Yes	Sample must be conditioned to lower water vapor.	411, 441
DuPont Model 460	Nondispersive UV: A beam flight is passed through the sample, then split and monitored by two phototubes, one monitoring a reference wavelength and the other a non-absorbing wavelength.	SO ₂	0 to 100 ppm (0 to 100%)	5 ppm	No	Yes	-	441, 442
Barringer Res. Ltd. Cosper II	Correlation Spectroscopy: Instrument consists of two telescopes, a two-grating spectrometer for dispersion, a disc shaped multiple-slit mask, and electronics. Disk mask is a high contrast reference spectrum for correlation against incoming absorption spectra and is comprised of arrays of circular slits photo-etched in aluminum on quartz. Photomultiplier tubes detect light modulations produced by rotation of disc. Unit continuously measures optical depth in ppm-meters of gas cloud under observation and uses diffused sunlight as a source of radiation.	SO ₂	1 to 1000 ppm meters	6 ppm meters	No	Yes	There are slight interferences due to changes in sky spectral distribution. Light scatter from particulates might cause interpretation problems.	450

TITLE CONTINUOUS MONITORING OF SULFUR DIOXIDE (CONTINUED)

ID NO. 02-05-02-03

Table 02-05-02-03B. Reference for SO₂ Continuous Monitors

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- 443 Stevens, R.K., L.F. Ballard and C.E. Decker, "Field Evaluation of Sulfur Dioxide Monitoring Instruments," U.S. Environmental Protection Agency, Air Pollution Control Office, Raleigh, N.C.
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1. TITLE CONTINUOUS MONITORING OF CO/CO ₂		2. IDENTIFICATION CODE 02-05-02-04
3. ABSTRACT OF METHODOLOGY		
Table 02-05-02-04A summarizes representative CO/CO₂ instruments. The recommended method for fugitive emission and flue gas monitoring is NDIR. With the proper conditioning, the NDIR unit will provide accurate and rapid response. The Beckman Model 866 has been designated a reference method for ambient CO measurements.		
4. APPLICATION: All areas.		
A) OPERATIONAL SCOPE See Table 02-05-02-04A. B) INTERFERENCES/LIMITATIONS See Table 02-05-02-04A. C) RECOMMENDED USE AREA See Abstract of Methodology.		
5. OPERATIONAL PARAMETERS See Table 02-05-02-04A.		
A) RANGE B) ACCURACY C) PRECISION		
6. REAGENTS REQUIRED	7. EQUIPMENT REQUIRED	
Calibration gases.	See Table 02-05-02-04A.	
8. KEYWORD INDEX: Analysis, continuous monitoring, CO, CO ₂ .		
9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02, 03, 04.		
10. REFERENCES See Table 02-05-02-04B.		
A) PRIMARY SOURCE B) BACKGROUND INFORMATION C) FIELD APPLICATIONS		

Table 02-05-02-04A. Summary of Representative Instruments for Continuous On-Line Monitoring of CO/CO₂.

Manufacturer/ Model	Principle of Operation	Species Monitored	Range	Sensitivity	Fugitive Emissions	Flue Gas Emissions	Interferences/ Remarks	Ref.
Bacharach Model US 400L	Mercury Substitution - Ultraviolet Absorption: The heterogenous reaction between carbon monoxide and mercuric oxide is utilized to generate mercury vapor in the sample gas stream at a concentration proportional to the original CO concentration. Ultraviolet photometry is used to measure the Hg vapor specifically and with great sensitivity.	CO	0-500 ppm	0.05 ppm	Yes	No	Other gases can release the Hg and must be scrubbed from the sample gas before contact with the HgO.	453, 466
Beckman Model 866	NDIR: Differential absorption of infrared energy measured by a selective gas microphone detector in a dual beam optical system.	CO	0-50 ppm	0.4 ppm	Yes	No	Solid, rugged method of CO monitoring. H ₂ O vapor should be removed for most accurate results.	568, 052, 452, 454, 466, 467
Enviro-Metrics Model C-328	Electrochemical cell: Some of the sample gas molecules diffuse through a membrane and dissolve in a thin film covering a sensing electrode. Electrooxidation or reduction occur at this electrode. The current is monitored versus a reference electrode and related to the gas of interest.	CO	0-10,000 ppm (Range variable)	1% full scale	Yes	Yes	Sample conditioning is essential to operation of instrument. Water, SO ₂ , and NO ₂ must be removed.	455, 466
Environmental Data 1 Diga Series	Absorption Spectroscopy: Long path in stack absorption of IR radiation at 4.7 μ for CO and 4.25 μ for CO ₂ .	CO/CO ₂	0-1000 ppm (2 ranges)	N/Q	No	Yes	Sulfur dioxide, NO, CO ₂ and opacity can also be measured.	456, 457, 466
Mine Safety Appliances Model D	Catalytic Oxidation: A sample of air is drawn through two beds of active and inactive Hopcalite. Thermistors in each bed monitor the heat of oxidation of CO to CO ₂ .	CO	0-500 ppm	N/Q	Yes		Interferences (SO ₂ , NO, and water) must be removed before sample is introduced into the cell.	459, 460, 461, 466
Philips	Amperometric: Dust and interfering gases are removed from the sample gas stream. The CO reacts with an active element (iodine pentoxide) in an electrolytic cell. The change in concentration of the active element generates a current which varies directly as the concentration of the gas component being measured.	CO	0-200 (4 ranges)	0.1 ppm	Yes	No	By proper choice of prefilters this unit can also measure SO ₂ , NO _x , O ₃ and H ₂ S. Interferences from these gases are less than 1%, but require careful conditioning of interference absorbant column.	458, 462
Wilks Model 5630	Dispersive IR: This instrument consists of a variable IR range from 2.5 to 14.5 μ and variable path gas cell from 3/4 to 20 meters. The CO absorbance at 4.7 μ or the CO ₂ absorbance at 4.25 μ is monitored.	CO/CO ₂	0-8.3%	1.2 ppm	Yes	Yes	Water should be eliminated by the use of drying agents. Contributions by other interferences (N ₂ O, H ₂ S, olefins, cyanogens, etc.) can be subtracted from the CO/CO ₂ absorbance by scanning the 2 to 14 μ spectrum.	458, 463, 464, 465, 467

TITLE CONTINUOUS MONITORING OF CO/CO₂ (CONTINUED)

ID NO. 02-05-02-04

Table 02-05-02-04B

Continuous On-Line Instruments for CO/CO₂ Monitoring

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- 052 Leithe, W., "The Analysis of Air Pollutants," Ann Arbor-Humphrey Science Publishers, London, 1970, p. 63-68.
- 454 Parts, L.P., P.L. Sherman, and A.D. Snyder, "Instrumentation for the Determination of Nitrogen Oxide Control of Stationary Source Emission," Vol. 1, Report of the Monsanto Research Corp., Dayton, Ohio, prepared for the Office of Research and Monitoring, EPA Publication APT-0847 (Oct. 1971), p. 15-22.
- 455 "Plug-In Sensors In Membranes Put Finger on Inter Pollutants," Prod. Eng., 41, 40 (1970).
- 456 Lord, H.C., et al., "Instantaneous, Continuous, Directly On-Stream Boiler Flue Gas Analysis," presented at the Instruments Society of America, 24th Annual Power Industry Symposium, New York City, N.Y. (May 17, 1971).
- 457 Rosenthal, K., and R.J. Ambeck, "Continuous Monitoring of Stack Gases," presented at the Instrument Society of America, 18th Annual Analytical Instrument Division Symposium, San Francisco, California (May 3, 1972).
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- 467 "Collaborate Reference Method for Continuous Measurement of Carbon Monoxide in the Atmosphere (Non-dispersable Infrared Spectrometry)," NTIS #PB-211-265, May 1972.
- 568 Fed. Reg., 41, 3624 (1976).

2. IDENTIFICATION CODE

02-05-02-06

1. TITLE CONTINUOUS MONITORING OF H₂S

3. ABSTRACT OF METHODOLOGY

Table 02-05-02-05A summarizes the representative equipment for H₂S monitoring. The recommended method for fugitive emissions is a GC with a FP detector because of the high sensitivity normally required. For flue gas measurements, the electrochemical instrument is recommended.

4. APPLICATION: Engineering evaluation R&D, environmental assessment.

A) OPERATIONAL SCOPE

See Table 02-05-02-05A.

B) INTERFERENCES/LIMITATIONS

See Table 02-05-02-05A.

C) RECOMMENDED USE AREA

See Abstract of Methodology.

5. OPERATIONAL PARAMETERS See Table 02-05-02-05A.

A) RANGE

B) ACCURACY

C) PRECISION

6. REAGENTS REQUIRED

Calibration gases.

(Note: AIRCO's aluminum containers are recommended for storage)

7. EQUIPMENT REQUIRED

See Table 02-05-02-05A.

8. KEYWORD INDEX: Analysis, continuous monitoring, H₂S.

9. CROSS REFERENCE ID NUMBERS 02-05-01-01, 02-05-01-02, 02-05-01-03, 02-05-01-04; 01-01; 01-05.

10. REFERENCES See Table 02-05-02-05B.

A) PRIMARY SOURCE

B) BACKGROUND INFORMATION

C) FIELD APPLICATIONS

TITLE CONTINUOUS MONITORING OF H₂S (CONTINUED)

ID NO. 02-05-02-06

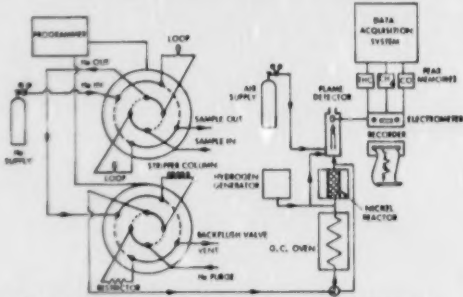
Table 02-05-02-05A. Representative H₂S Continuous Monitors.

Manufacturer/Model	Principle of Operation	Species Monitored	Range	Sensitivity	Fugitive Emissions	Flue Gas Emissions	Interferences/Remarks	References
Enviro-metrics Model S-390	Electrochemical cell: Some of the sample gas molecules diffuse through a membrane and dissolve in a thin film covering a sensing electrode. Electrooxidation or reduction occurs at this electrode. The current is monitored versus a reference electrode and related to the gas concentration.	H ₂ S	0-5000 ppm (3 ranges)	1% full scale	Yes	Yes	Source sampling requires sample conditioning to remove water and particulate	447, 468
Phillips	Coulometric: The sample, cleaned of particulate and conditioned via selective filters, is introduced into a measuring cell. The H ₂ S reacts with the active element in the electrolyte changing the concentration of the active element. This generates a current which varies directly with the H ₂ S concentration.	H ₂ S	0-10,000 ppb (3 ranges)	10 ppb	Yes	No	Care must be taken in ensuring that interfering gases such as SO ₂ or NO _x are removed or compensated for in the final analysis.	469, 470
Technicon Air Monitor IV	Coloumetric: H ₂ S in the gas stream is reacted in a flowthrough cell with p-aminodimethyl-aniline and FeCl ₃ to produce a colored product whose absorbance is monitored at 660 nm.	H ₂ S	0-200 ppb	2 ppb	Yes	Yes	Selective removal of SO ₂ , NO _x , O ₃ required for specific results	471, 472
Tracor 270H Analyzer	GC - Flame Photometric Detector: The sample is eluted from the gas chromatographic column, mixed with air and burned in an H ₂ rich flame. The decomposition of the sample in this flame gives a characteristic optical emission at 394 nm.	H ₂ S, S ₂ , RSH	0-1 ppm (variable)	5 ppb	Yes	Yes	Not truly continuous, but sample injected automatically on column at pre-selected times allows analysis of all sulfur compounds	465, 473, 474

Table 02-05-02-05B.

List of References Concerning Continuous Monitors for Hydrogen Sulfide Emissions.

- 447 "Plug-in Sensors in Membranes Put Finger on Air Pollutants," *Prod. Eng.*, 41(26), 40 (1970).
- 468 Chand, R., and R.V. Marcote, "Evaluation of Portable Electrochemical Monitors and Associated Stack Sampling for Stationary Source Monitoring," presented at the 68th National Meeting of the American Institute of Chemical Engineers, Houston, Texas.
- 469 Washburn, H.W., and R.R. Austin, "The Continuous Measurement of Sulfur Dioxide and Hydro Sulfide Emissions by Automatic Titration," Chapter 72 in *Air Pollution Proceedings of the U.S. Technical Conference on Air Pollution*, L.C. McCabe (Chairman), McGraw-Hill, New York, 1952.
- 470 R.R. Austin, G.H. Dehaas, and G.N. Thoen, "Instrumentation for Quantitative Measurement of Sulfur Compounds in Flue Gases," *Tappi (Journal of the Technical Assoc. of Pulp and Paper Industry)*, 51, 246 (1968).
- 472 Rodes, C.E., et al, *J.A.P.C.A.*, 19, 575 (1969).
- 472 Palmer, H.F., et al, *J.A.P.C.A.*, 19, 778 (1969).
- 473 Stevens, R.K., and A.E. O'Keefe, *Anal. Chem.*, 42, 143A (1970).
- 405 Decker, C.E., T. Royal and J. Tommerdahl, "Field Evaluation of New Air Pollution Monitoring Systems," Final Report of Research Triangle Institute, Research Triangle Park, N.C., EPA Contract No. EPA-70-101, May 1972.
- 474 Ballard, L.F., et al, "Field Evaluation of New Air Pollution Monitoring Systems: The Los Angeles Study," Interim Report of Research Triangle Institute, Research Triangle Park, N.C., EPA Contract No. 70-101, EPA Publication APED-0775, April 1971.

1. TITLE DETERMINATION OF HYDROCARBONS CORRECTED FOR METHANE	2. IDENTIFICATION CODE 02-05-02-06
3. ABSTRACT OF METHODOLOGY	
Method involves use of hydrogen flame detector to measure total hydrocarbon content, and a gas chromatograph to measure methane. Figure 02-05-02-06 shows a typical apparatus flow diagram. An aliquot of collected sample gas is treated for the removal of water, CO₂, and nonmethane hydrocarbons in a stripper column. Methane and CO are allowed to pass through a GC column for separation. The eluted methane is then passed through a catalytic reduction tube into a flame ionization detector. The CO is then eluted into the tube and reduced to methane, then is passed into the flame ionization detector. The hydrocarbon content is corrected for methane by subtracting the methane value from the total hydrocarbon value.  Figure 02-05-02-06. Schematic of GC operation	
4. APPLICATION: Compliance.	
A) OPERATIONAL SCOPE Method is applicable to semi-continuous measurement of hydrocarbons corrected for methane in ambient air. B) INTERFERENCES/LIMITATIONS No interferences have been observed for methane measurement. Air peak interferences can be minimized by mechanical methods or can be electronically negated. C) RECOMMENDED USE AREA	
5. OPERATIONAL PARAMETERS	
A) RANGE. The range is 0-13.1 mg/m³ (0 to 20 ppm) carbon as CH₄ and 0.655 mg/m³ methane for atmospheric analysis. Lower ranges (0-1.31 mg/m³ or 0 to 2 ppm carbon as CH₄, and 0 to 1.31 mg/m³ methane) are available for special applications. B) ACCURACY 1% of full scale in higher atmospheric analysis range, and 2% of full scale in lower special analysis ranges. C) PRECISION ±0.5%.	
6. REAGENTS REQUIRED Combustion gas, fuel, carrier gas, zero gas, calibration gas, span gas.	7. EQUIPMENT REQUIRED Commercially available total hydrocarbon analyzer, sample introduction system, filter, stripper or pre-column, oven.
8. KEYWORD INDEX: Hydrocarbons, ambient air, compliance.	
9. CROSS REFERENCE ID NUMBERS 02-05-01, 02-05-02-04.	
10. REFERENCES	
A) PRIMARY SOURCE 480 U.S. Environmental Protection Agency, "Reference Method for Determination of Hydrocarbons Corrected for Methane," Title 40, Part 50, Chapter I, Subchapter F, Appendix E, Washington, 1971, p. 21. B) BACKGROUND INFORMATION 527 Fee, G., "Multi-Parameter Air Quality Analyzer," ISA Proceedings, AIO/CHEMPID Symposium, Houston, Texas, April 19-21, 1971. 528 Stevens, R.K., and A.E. O'Keeffe, Anal. Chem., 42, 143 A (1970). 529 Stevens, R.K., A.E. O'Keeffe and G.E. Ortman, "A Gas Chromatographic Approach to the Semi-Continuous Monitoring of Atmospheric Carbon Monoxide and Methane," Proceedings of 11th Conference on Methanes of Air Pollution on Industrial Hygiene Studies, Berkeley, California, March 30-April 1, 1970. 530 Instruction Manual for Air Quality Chromatograph Model 6800, Beckman Instrument Co., Fullerton, California. 531 Instruction Manual, Bendix Corp., Ponceville, W. VA. C) FIELD APPLICATIONS	

1. TITLE CONTINUOUS ON-LINE LIQUID ANALYSIS WITH A TECHNICON MONITOR IV SYSTEM		2. IDENTIFICATION CODE 02-05-03-01
3. ABSTRACT OF METHODOLOGY		
The Monitor IV system is a continuous on-line system for wet chemical analysis of water. The system operates on the principle of continuous flow analysis, where air segmented streams of sample and reagents are brought together and reacted under carefully controlled conditions. The resulting color, or color reduction, is measured by a beam of light as the analytical stream passes through a colorimeter.		
4. APPLICATION: Engineering evaluation R&D.		
A) OPERATIONAL SCOPE This equipment is designed to monitor industrial streams before and after water treatment. Instruments are available for: Ortho Phosphate, Silicates, Cyanide, Ammonia, Nitrate and Nitrite, Copper, Cr (VI), Chloride, Hardness, Total Iron, Hydrazine, Total Inorganic Phosphate. B) INTERFERENCES/LIMITATIONS Water clarity and color can affect instrument response. Preventive maintenance should be performed at seven-day intervals. Wet analysis should be verified manually prior to automatic analysis. C) RECOMMENDED USE AREA This instrument is the recommended instrument for continuous on-line liquid analysis for engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE Depends on analysis performed (ppb to ppm). B) ACCURACY Depends on analysis performed (± 10 to $\pm 25\%$ estimated). C) PRECISION $\pm 2\%$.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Depends on analysis performed.		Technicon Monitor IV system (Technicon Instruments Corp., Tarrytown, New York).
8. KEYWORD INDEX: Analysis, continuous, liquid on-line analysis.		
9. CROSS REFERENCE ID NUMBERS 02-03-02- (see specific wet chemical tests).		
10. REFERENCES		
A) PRIMARY SOURCE 475 Technicon Industrial Systems, "Specifications and Engineering Standards: M-IV," February 19, 1973. 476 Technicon Industrial Systems, "Specifications and Engineering Standards: M-IV/A-1:2, 17A, 301, 212, 177, 207, 215, 255, 251, 305 and 147," January through May 1975. B) BACKGROUND INFORMATION C) FIELD APPLICATIONS		

1. TITLE CONTINUOUS ON-LINE MONITORING OF LIQUID STREAMS WITH ORION SPECIFIC ION ELECTRODES		2. IDENTIFICATION CODE 02-05-03-02
3. ABSTRACT OF METHODOLOGY The Orion series 1000 process stream monitor employs a specific ion electrode system to continuously monitor a process stream. The instrument uses reagents which eliminate both electrode and method interferences. The monitor consists of a sensing electrode and tag ion electrode (TIE) in a thermostatic flowthrough cell. The TIE is a second specific ion electrode which is responsive to a tag ion (for example Na⁺) present in the reagent in sufficient quantities to swamp out the effect of any tag ion in the process stream. Proportioning pumps supply filtered sample and reagent to a flowthrough cell where the measurement is made. The output is displayed on a meter or strip recorder. Reagent supplies and automatic re-standardization allow unattended operation up to 60 days.		
4. APPLICATION: Engineering evaluation R&D, environmental assessment.		
A) OPERATIONAL SCOPE Present units are designed to monitor CN ⁻ , NH ₄ ⁺ , halide ions, metal ions, water hardness, residual chelant, total acid and total base. These units are designed to operate in industrial plant environments to control process streams or monitor pollution levels in industrial waste streams.		
B) INTERFERENCES/LIMITATIONS Suspended solids can foul electrodes, but the bypass filter system is designed to reduce that problem. Reagents are designed to eliminate interferences, but each electrode/stream combination should be studied to ensure accurate readings.		
C) RECOMMENDED USE AREA Process or pollution monitoring for engineering evaluation R&D.		
5. OPERATIONAL PARAMETERS		
A) RANGE Logarithmic response - 4 decades of concentration (detection limits depend on electrode).		
B) ACCURACY N/Q (±10%).		
C) PRECISION ±5% over 4 decades.		
6. REAGENTS REQUIRED		7. EQUIPMENT REQUIRED
Depends on species monitored.		Orion Series 1000 continuous chemical monitor (Orion Research, Cambridge, Mass.).
8. KEYWORD INDEX: Analysis, continuous liquid analysis.		
9. CROSS REFERENCE ID NUMBERS 02-03-02-01.		
10. REFERENCES		
A) PRIMARY SOURCE 477 Orion Research, <u>Newsletter</u> , 5(1), 1973.		
B) BACKGROUND INFORMATION		
C) FIELD APPLICATIONS 478 Riseman, J.H., "Electrode Techniques for Measuring Cyanide in Waste Waters," <u>Am. Lab.</u> , 4(12), 63 (1972). 479 Thomas, R.H., and R.L. Booth, "Selective Electrode Measurement of Ammonia in Water and Wastes," <u>Environ. Sci. Tech.</u> , 7(6), 523 (1973) (see 02-03-02-01 for further references).		